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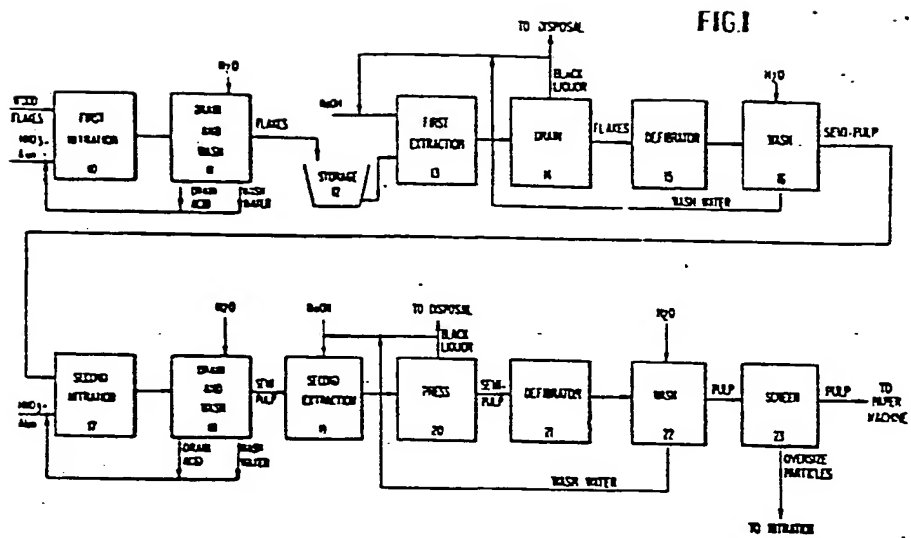
54 A process for treating fibrous ligno-cellulose material to form defibred pulp material by an accelerated pulping process and a fertilizer composition comprising said ligneous material.

57 A process for making defibred pulp material comprising the steps of treating fibrous ligno-cellulosic material with aqueous nitric acid (10,17) having an HNO<sub>3</sub> concentration of about 0.15 to 9.0 wt.% and containing aluminium sulphate in an amount of about 0.8 to 1.3 parts per each 10 parts by weight of HNO<sub>3</sub>, or to alternatively use for grassy fibrous materials nitrate salts such as NaNO<sub>3</sub> or KNO<sub>3</sub> or NH<sub>4</sub>NO<sub>3</sub>, so as to nitrate ligneous component of said material; and thereafter defibering directly, (15,21) or treating the nitrated ligno-cellulosic material with alkali to separate the ligneous component from the cellulosic pulp, and, optionally, recombining a part or all of the ligneous component with the cellulosic pulp. (Figure 1).

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BAD ORIGINAL





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Accelerated Pulping Process

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This invention relates to an improved process of making fibre in a form ranging from a moderately digested product  
5 fit for animal feed to pulps that can be utilized as conventional semi-chemical, chemical types for packaging papers or fully delignified pulps for bleaching from fibrous, ligno-cellulosic raw material, More particularly, it relates to a nitration pulping process using nitric  
10 acid or nitrate salts in which the time required for nitration and the second step extraction of the nitrated ligneous components in the fibrous raw material is substantially shortened due to the inclusion in the nitric acid of a small amount of aluminium sulphate (paper maker's alum),  
15 and by use of the inherent flexibility of the process time, temperature and chemical concentration, the utilization of controlled delignification to produce animal feed, building board, packaging boards and paper.

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So far as I am aware, nitric acid pulping processes, of which many have been proposed, have never been commercially  
5 successful for various reasons, chief among which is the relatively long chemical treatment time that they required far exceeding the present day conventional methods. Shortened times were possible if strong nitric acid was used, or if pressurized vessels and high temperatures were  
10 employed, but those conditions create other problems such as excessive and explosive emission of toxic nitrogen oxide fumes and damage to the cellulosic fibre structure. Moreover, recovery of the acid has not been possible, and the use of relatively concentrated nitric acid, e.g. 15 to 42  
15 % by wt.  $\text{HNO}_3$ , becomes therefore prohibitively expensive. In short, the nitric acid pulping processes heretofore proposed have offered no advantages and many disadvantages over present day conventional systems. As recently as 1960  
20 a published comprehensive review on nitric acid pulping by Crown Zellerbach Corporation stated that while nitric acid was specific for the reaction with lignin; the use of acid reagent was excessive and uneconomic, and pollution problems remained unsolved.

25 The process of this invention uses only 0.15 - 9.0% nitric acid in relation to fibre yield which, together with the alkali used for delignification, is no more than with conventional methods of pulping without chemical recovering systems while eliminating the complex requirements of recovery and/  
30 or manufacture of the cooking liquors. Furthermore, since the process is a two step one, the nitrating solution can, except for that absorbed in the fibre structure, be recovered virtually intact and recycled. More importantly, unlike previous attempts with nitric acid, this new process  
35 does not dissolve the lignin content of fibrous structures in the acid stage.

Conventional pulp mills require high investment due to the

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high temperatures and pressure involved, and if water and  
air pollution is controlled and chemical recovery is prac-  
5 ticed costs are substantially higher. The process of this  
invention uses simple chemicals available in crystalline  
or dissolved form, does not require superatmospheric  
pressure, or temperatures over 100°C, offers minimal pro-  
blems of air and water pollution, and offers economic usa-  
10 bility of the products normally wasted by burning or  
dumping.

I have now discovered that in a chemical pulping process  
involving impregation of particulate, fibrous, ligno-  
15: cellulosic raw material with nitric acid which may be or  
not be followed by alkaline extraction from the material  
of the resulting nitrated lignin, leaving softened, parti-  
ally defibered cellulosic structures which can be complete-  
ly defibered by mechanical pulping means, the total time  
20 required for the nitration and extraction steps can be  
shortened considerably by including a small amount of  
aluminium sulphate (paper maker's alum) in the nitric  
acid.

25 While the precise time required for the nitration-extrac-  
tion operation is dependent upon the variables of particle  
thickness, temperature and reagent concentration, it can  
be said for the process of the present invention that it  
generally enables one to perform the nitration-extraction  
30 operation somewhere in the range from about 20 minutes  
minimum for high yield wood chemical pulps for packaging  
papers and boards, to a maximum time of 50 minutes for  
easily bleached pulps without using pressure and with  
temperatures not exceeding 100°C. Those times are to be  
35 compared to the conventional sulphite process times of  
6.25 hours and 7.50 hours and the sulphate process times  
of 2.5 and 5.0 hours, respectively, at high pressures and  
temperatures, as set forth in the following table I:

Table I

## Pulping Processes Compared

	Liquor Concentration, Wt. %	Total Cooking Time	Temperature, °C	Pressure, P.S.I.G.	Fibre Species	Total Yield, %
1. Casey, "Pulp and Paper" Vol. 1, p. 169						
<u>Sulphite-Bleach Grade</u>						
Calcium Base	6.0	6.25 hrs.	140	80	Western Conifer	45.4
Ammonia Base	6.0	7.50 hrs.	146	80	Western Conifer	45.0
2. Casey, pp. 230-264						
Sulphate - High Yield	18.5	2.50 hrs. (1)	170	140	U.S. So. Pine	60.0
Sulphate - Bleachable (1) includes time to bring to temperature	22.0	5.00 hrs. (1)	160	100	U.S. So. Pine	43.0
3. TAPPI CA Report, 52 pp. 17-19						
Bagasse - Soda Process (2) includes cooking time in blow tank	6.5	26.50 min. (2)	170	114	Bagasse	56.0
4. TAPPI CA Report 52, pp. 26-27						
Bamboo - Kraft Process	17-19	1.25 hrs.	150	85	Bamboo	56.0
5. Accelerated Pulping Examples (Invention)						
High Yield Grade	HNO <sub>3</sub> / NaOH 5.5 / 0.3	30 min.	85-100	None	U.S. So. Pine	56.0
Bleachable Grade (1st sequence)	3.0 / 0.3	30 min.	85-100	None	Norway Spruce	45.0
(2nd sequence)	1.5 / 0.1	20 min.	85-100	None		
Bagasse	0.8 / 0.2	30 min.	85-100	None	Bagasse	52.0
Bamboo	3.0 / 0.2	30 min.	85-100	None	Bamboo	44.0



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Although the invention is described below mainly referring  
to the embodiment involving an alkaline extraction of ni-  
5 trated lignin after the nitration step, it is recognized  
that, though preferable, an alkaline extraction is not  
absolutely necessary for the production of paper pulps.  
However, the addition of alkali is necessary for the pro-  
duction of animal feeds and would be normally used in the  
10 production of semi-chemical pulp where maximum defiberiza-  
tion for minimum chemical treatment is desired.

The ability of the present process to be conducted under  
atmospheric pressure eliminates the need of explosive re-  
15 lease of pressure that is used in conventional chemical  
pulp systems to defibre the fibrous structures within chips  
or chopped materials. The basic preservation of the fi-  
brous structure permits easy recycling of the fibrous  
structure through an additional gentle cooking cycle, if  
20 required, and easy drainage of cooking liquor and washing  
out of the residual black liquor leaving the fibrous struc-  
ture substantially intact. Defiberization is then accompi-  
shed mechanically with gentleness and rapidity, with mini-  
mum loss of fibre length and degradation of basic fibre  
25 structure. Additionally, the defiberization can be closely  
controlled to preserve long thin fibre bundles from fibrous  
structures made up of very short (under 0.5mm) fibres such  
as straw thus improving strength and drainage characteristics.

30 All forms of ligno-cellulosic materials can be subjected  
to the pulping process of the present invention. That in-  
cludes, without limitation, woody materials such as U.S.  
Southern pine, spruce, beech and bamboo, as well as grassy  
materials which find minor usage such as straws, bagasse  
35 and kenaf. In addition to these normally used sources of  
paper making fibre, other, now wasted, fibrous plants as  
rape seed straw and rice husks which resist conventional  
pulping methods can easily be reduced to potentially useful

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fibre by this process. High yield shrub growth such as coppice willow found extensively in Ireland and presently unused produces, including its bark, an acceptable, clean and economic paper making fibre. Besides such virgin materials, the process of the present invention can be used to delignify and further defibre paper wastes, such as waste corrugated boxes containing semi-chemical board.

10 Finally, it becomes practical to economically pulp small accumulations of wood slab waste and sawdust which are most often burned.

The raw material should be in particulate form before being submitted to the nitration step. Virgin plant material, for example, should be chopped, crushed, chipped or flaked. Paper wastes should be mechanically pulped in water to the defibered state, for example to obtain a slurry containing about 7 to 9 wt.% cellulose. When it is wood that is to be pulped, the required nitration extraction time will be shorter and the pulp more uniform if the wood particles are thinner. It has been found especially advantageous to use wood flakes, i.e. particles about 0.3 to 0.8 mm thick obtained by cutting the log tangentially to the circumference. Flaking is the cutting process used in manufacturing particleboard. At the present time the paper manufacturing industry uses wood chips almost exclusively, the thickness of which is usually in the range of about 6 to 10mm. Horsepower consumption for the flaking of logs is roughly equivalent to that for chipping, as are production levels and flexibility in handling short or long or different diameter logs. The use of flakes does require higher cubic handling and cooking capacities than does chips, but flaking is nonetheless economically acceptable in the pulping process of this invention because high pressure pressurized cooking vessels with restricted volumes are not required.

Use of wood flakes, rather than the thicker chips, speeds

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nitric acid impregnation and also shortens the time re-  
quired for outward diffusion of dissolved lignin in  
5 the subsequent alkaline extraction step. Additionally,  
flaking is accomplished by cutting around the circumference  
of the log, much as veneers are made, whereas chipping is  
performed by cutting at the end of the log, the fibre  
length is essentially preserved in flakes and the fibre  
10 ends are not crushed. Chipping, on the other hand, fractu-  
res the fibres and crushes their ends. The more intact fi-  
bre structures and greater exposed surface of the flakes  
are more easily penetrated by the chemicals used in the  
nitration and extraction steps of the present process. The  
15 fibres produced from flakes are marginally shorter than  
those of conventional chips.

Where a pulp is required for rough papers, i.e. brown or  
packaging papers and boards, conventional chips can be  
20 used after subjecting them to conventional crushing which  
reduces them to rough splinters 1.5 - 3.0mm thick, 4.0 -  
8.0mm side and 25mm long.

The nitration (cooking) of the ligno-cellulosic raw material  
25 is accomplished by submerging or wetting with recycled acid  
the material in a sufficient amount of aqueous nitric acid  
at elevated temperature, preferably 85 to 100°C to pene-  
trate the fibrous structure and react with the lignin.  
In order to permit the use of an open vessel for the ni-  
30 tration step, without the emission of harmful nitrogen oxi-  
de vapors, it is preferred to use very dilute nitric acid,  
say having an  $\text{HNO}_3$  concentration of about 0.15 to 9.0  
weight percent, e.g. 0.15 to 5.5 weight percent, preferably  
less than 5.5 weight percent and most preferred less than  
35 5 weight percent. It can be preferred to subject the ligno-  
cellulosic raw material to an impregnation step before the  
cooking-nitration step. The impregnation is done with a  
dilute concentration of the cooking liquor at low tem-

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peratures (e.g. 70°C or below, e.g. 50°C or below) and serves three purposes:

- 5 a) Utilization of drained concentrated liquor after the cooking process together with the dilute cooking liquor from the washing process,  
b) conservation of heat by recycling liquor, and  
c) even moisture distribution throughout the fibrous  
10 structure before cooking.

Whereas the cooking step is not necessarily preceded by an impregnation step, an impregnation step is always followed by a cooking step.

- 15 The preferred acid strength in the cooking-nitration step depends upon the nature of the ligno-cellulosic raw material being pulped. For U.S. Southern pine, for example, which is relatively high in lignin content (over 30 wt.%), and contains a high percentage of resins and waxes it is  
20 preferred to use an  $\text{HNO}_3$  concentration of at least 4.5 or 5.5 wt.%. Wheat straw, on the other hand, is low in lignin content (about 15 wt.%) and is preferably cooked and nitrated with nitric acid having an  $\text{HNO}_3$  concentration of only about 0.8 to 1.5 wt.% for production of chemical pulp. These con-  
25 centrations are based on a normal nitration period of 15 minutes and production of chemical type pulp.

- Where impregnation periods and longer time is used the acid concentration can be drastically reduced. For example,  
30 spruce flakes-impregnation 30 minutes at 0.5% concentration plus cooking and nitration, respectively, 45 minutes at 1.75%. Where a pulp of lower purity (i.e. less delignification) is required the said concentration can be reduced, as in animal feed or semi-chemical pulp. As a practical  
35 matter it will usually be woody plant material that is twice subjected to the cooking-nitration/lignin-extraction sequence, since grassy plant materials and paper wastes can have their ligneous components nitrated and almost

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completely extracted in one sequence using relatively stronger, but still dilute, nitric acid, and obtain pulp of adequate cellulosic purity and easy bleachability. Even with woody raw materials, a single nitration-extraction sequence is all that is required where the pulp product is to be used to make linerboard and lower brightness papers and not to make high purity cellulose or high brightness paper.

In the process of the present invention the nitric acid impregnation liquor is augmented with a nitration accelerating amount of aluminum sulphate, preferably about 0.8 to 1.3 parts thereof per each 10 parts by weight of  $\text{HNO}_3$ . As stated above, the presence of the aluminum sulphate in the nitric acid serves to shorten dramatically the time required to dissolve the nitrated lignin in the subsequent alkaline extraction step. Normal usage is 1.0 part of the aluminum sulphate per each 10 parts by weight of  $\text{HNO}_3$ . (100%).

The amount of nitric acid used in the nitration step should be sufficient to completely react by submergence or contact by recirculation the particulate ligno-cellulosic material and adequate on a stoichiometric basis to nitrate all of the lignin content of the raw materials. This will usually mean formation of a mixture of 5 parts of liquid acid to 1.0 part of dry wood to 10 parts of liquid acid for 1.0 part of dry grass fibre (straw). Where the acid liquor can be circulated and heated indirectly lower ratios can be used. Additionally the acid can be sprayed or foamed in low concentration on grassy fibres to form an intimate mixture to a composite moisture content of 35 to 50% and then subjected to heat for reaction at once or at later date - six months or more without degradation.

The temperature at which the nitric acid cooking step is

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performed should be adequate to effect nitration of the lignin, but is preferable not so high as to cause degradation of the cellulosic fibres. Temperatures within the range of about 85 to 100°C, in particular about 85 to 95°C, are preferred. Since the nitration-extraction portion of the process of the present invention can be performed in such a short period of time, it is possible to conduct both of those steps under atmospheric pressure conditions, although superatmospheric pressures, e.g. from 10 to 35 p.s.i.g., can be used if it is desired to shorten the nitration time slightly but chiefly to provide ease of processing on a continuous basis. The improvement provided by the present invention is independent of whether the process is conducted under atmospheric pressure or at elevated pressures.

The introduction of a non pressure system is designed specifically for use in new and relatively small pulping installations (10 - 50 tons per day) throughout the world. However, it is recognized that the requirement for larger production units can be met and that in many instances existing pulp mill equipment could be utilized to reduce investment costs in preventing present pollution problems.

All present systems use high pressures and temperatures coupled with long cooking periods for fully defibered or chemical pulps from either wood or grasses. It has been found that by cooking with light pressures (15-35psig) while holding temperatures at 110°C or below, preferably below 100°C (most preferably 95°C) the nitration period can be shortened to 5 - 7 minutes for wood flakes, straw, etc. Conventional sized wood chips can also be readily pulped although the cooking time period is extended to one hour requiring two nitration steps with a preliminary defibering step between. Alternatively, the chips can be crushed previous to filling the

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digester and the nitration step limited to one step which additionally avoids the possibility of over and under reacted fibrous structures. These methods of using light pressures with either wood flakes or chips makes practical, for example, the conversion of existing sulphite pulp mills to this process. Other pulping systems such as the "Kamyr" or "Pandia"-system, which are continuous, operating at high pressure, 150 - 175 psig, are also adaptable for processing wood chips in one stage producing a semi-chemical type after normal mechanical defibering or full chemical pulp. Thus, in a special embodiment of the inventive process the nitration step is operated at a pressure of about 100 to 150 psig when using as starting material crushed wood chips as used in conventional processes today. See Table IIa "Comparative  $\text{HNO}_3$  Pressure Nitration Cycles . Normal Chemical or Delignified Pulp."

20 Additionally it has been found that the use of pressure permits full defibering of the fibrous structure in the nitration stage without production of black liquor thus avoiding the lignin alkali extraction phase. This is accomplished by raising the  $\text{HNO}_3$  liquor concentration by 2.5 - 3.5% over that required for the nitration-alkali delignification sequence and extending the time of reaction slightly, 3-5 minutes. Thus, without using pressure, i.e. conducting the process under approximately atmospheric pressure conditions, the  $\text{HNO}_3$  liquor concentration is preferably at most 5.5 weight percent, in particular at most 5 weight percent. When employing pressure, the  $\text{HNO}_3$  concentration can go up to 9.0 weight percent and preferably it is no more than 7.5 or 7.0 weight percent. Of course, the lower concentrations as stated for the pressurized nitration step can be advantageously used.

The process without delignification produces a fibre for different and limited end use papers than that of the

## Table IIA

Comparative HNO<sub>3</sub> Pressurized Nitration Cycles, Normal Chemical or Delignified Pulp with Alkali Stage

## A. Non Pressure System - Wood Flakes or Equivalent

Cooking Time	Minutes	Pine	Spruce	Beech	Straw
Temperature	°C	15	15	15	15
Liquor Concentration	%	85	85	85	85
		5.5	5.0	4.0	1.0

## B. Pressure 15 - 35 p.s.i.g. - Wood Flakes or Equivalent

Cooking Time	Minutes	Pine	Beech	Straw	Bamboo
Temperature	°C	7	7	5	7
Liquor Concentration	%	110	110	110	110
		5.5	3.5	0.5	2.5

## C. Pressure 15 - 35 p.s.i.g. - Wood Chips

Cooking Time	Minutes	Spruce	Beech
Temperature	°C	45	45
Liquor Concentration	%	110	110
Defiberization		4.5	3.5
Time - Non Pressure		x	x
Temperature	°C	15	15
Liquor Concentration	%	85	85
		2.5	2.0

## D. Pressure 100 - 150 p.s.i.g. - Wood Chips

Cooking Time	Minutes	Spruce	Beech	Beech
Temperature	°C	45	45	10
Liquor Concentration	%	110	110	110
Defiberization		4.5	3.5	3.0
		-	-	x

1 5 10 15 20 25 30 35



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delignified type fiber. It is of very light colour, high yield and can be easily bleached to high brightness levels, but not by normal alkaline bleaching. The reduced handling of the fibrous structure greatly improves its drainage properties and facilitates washing which is a major problem today in bleaching short fibre structures such as straw.

10 In all these uses of pressure it is not necessary to vent any gases; in fact it is economic that with the gases be contained and retained to create a false pressure and keeping operating temperatures below 100°C thus avoiding cellulose degradation. The degree of false pressure  
15 created is dependent on acid concentration.

See following Table IIb "Comparative  $\text{HNO}_3$  Pressure Nitration Cycles . No Delignification Stage." Where additional pressure is needed as in the "Kamyr"-process to facilitate  
20 operation it can be obtained with air injections.

The ability to conduct the nitration step at atmospheric pressure means that substantially open vessels can be employed providing substantial savings in equipment cost  
25 compared to conventional superatmospheric pulping processes. Although an open vessel can be employed for the nitration step, it is preferred to maintain closure with recycling of vapors to prevent possible troublesome emission of nitrogen oxide vapors. Present environmental laws in the  
30 U.S.A. permit a maximum nitrogen oxide emission level of only 185ppm. The precise temperature at which nitrogen oxide will be released from the slurry in the nitration step will depend upon the concentration of the nitric acid, since the higher the acid concentration, the lower  
35 will be the temperature at which nitrogen oxide vapor emissions will occur.

By way of further explanation, nitric acid decomposes at

Table IIb  
Comparative HNO<sub>3</sub> Pressurized Nitration Cycles, Alkali Delignification Stage Eliminated

<u>A. Pressure 15 - 35 p.s.i.g. - Wood Flakes or Equivalent</u>			
Cooking Time	Minutes	Pine	Chemical Pulp
Temperature	°C	10	Beech
Liquor Concentration	%	110	10
		9.0	110
			5.5
			6
			110
			2.5
			10
			110
			5.0
<u>B. Pressure 100 - 150 p.s.i.g. - Wood Chips</u>			
Cooking Time	Minutes	Spruce	Chemical Pulp
Temperature	°C	45	Beech
Liquor Concentration	%	110	45
		8.0	110
			5.5
<u>C. Pressure 35 - 150 p.s.i.g. - Wood Chips</u>			
Cooking Time	Minutes		Semi-Chemical Pulp Mixed Hardwoods
Temperature	°C		Beech
Liquor Concentration	%		10
			100
			4.0

1 5 10 15 20 25 30 35

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about 86°C into water and nitrogen oxide gas, which is potentially lethal and can be explosive. The nitrogen gas is somewhat soluble in water, however: about 130cc will dissolve in a litre of cold water, about 660cc will dissolve in a litre of hot water. If nitric acid having an  $\text{HNO}_3$  concentration greater than about 3.0 wt.% is heated in the presence of cellulose to above about 65°C then an exothermic reaction with the cellulose will result. For this reason, where an impregnation step becomes preferable to economize on nitric acid consumption through recycling of partly spent or diluted acid it is desirable to maintain low temperatures, e.g. 50°C or below. Temperatures over 85°C will produce nitrogen oxide gas which depending on the acid concentration will be more than the water can hold in solution and will have to be contained. When an open vessel is being used to conduct the nitration step in the process of the present invention, it will usually be preferred to employ a temperature no higher than about 90°C or 95°C. However, as stated herein before, when operating the nitration step under pressure a temperature of up to 110°C, preferably up to 100°C, can be employed.

25 It is an outstanding advantage of the process of the present invention that it can be performed in non-pressure vessels in short time periods, without causing air pollution problems.

30 The nitration step, and indeed the entire process of the present invention, can be carried out continuously, semi-continuously, or batchwise, whichever is desired. Selection of equipment will of course depend upon that choice. It is generally more economical to conduct the process continuously in which event the nitration step can advantageously be conducted in some type of screw conveyor unit. Batchwise nitrations can be carried out quite well in a hydropulper making possible the economic operation of very

small mills.

- 5 The nitric acid impregnation and cooking steps are conducted for a time sufficient to produce the required residual level of the ligneous component of the ligno-cellulosic raw material after extraction of the lignin. If the nitration-extraction sequence is performed twice, each nitration step can be conducted for a shorter period than if it were performed just once. The time required to effect the desired degree of nitration is dependent, of course, on the strength of the nitric acid used, as well as the temperature employed, since higher acid strengths and higher temperatures promote the nitration reaction.

Additional considerations are the type and particle size of the ligno-cellulosic material being processed. In general, with the process of the present invention the total nitration time, whether performed in one step or broken down into two nitration-extraction sequences, can be as short as 5 minutes or extended to 45 minutes. For straw or bagasse which will go into dry storage before lignification a simple spray or foam application at lower levels of acid concentration at room temperatures is all that is necessary. Following the nitration step the ligno-cellulosic material is separated from the nitric acid solution and preferably washed with water to remove surface acid. The wash water is preferably hot, e.g. at a temperature of about 85 to 100°C and is used in minimal amounts. One efficient method of separating and washing the nitrated ligno-cellulosic material is by spindraining the slurry in a rotary dryer, followed by water washing the solids in the same vessel. Another method, if a continuous system is used, is draining followed by reverse flow washing. Alternatively, draining, followed by flooding with wash water and a second draining can be used.

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The separated nitric acid is advantageously recycled to  
the nitration step to be used again, as is the acidic wash  
5 water. Both solutions will be relatively clear, but may be  
slightly coloured due to the presence of small amounts of  
dissolved material. The recycled nitric acid stream will  
be fortified with concentrated nitric acid and with  
fresh aluminum sulphate so as to restore the concentrations  
10 of those reagents to the desired levels.

The nitrated fibrous structures remain intact and appear  
to be essentially the same as when those particles were  
introduced to the nitric acid submersion step, except for  
15 some softening and a slightly darker colour. The nitrated  
fibrous structures can be held in storage for months with-  
out either deteriorating or causing problems in the lignin  
extraction and defibering steps which follow. This stora-  
bility feature can be of special advantage in the case  
20 where straw, bagasse or similar grassy plants are to be  
pulped. Grassy plants are usually harvested during rela-  
tively short seasons, causing temporary, seasonal surges  
in supply of that raw material to the pulp mills. Since  
the demand for the finished pulp is relatively constant,  
25 however, it becomes necessary to periodically store large  
quantities of the excess ligno-cellulosic raw material.  
This presents a problem because grassy plants are parti-  
cularly susceptible to bacterial or fungi attack during  
storage. By the process of the present invention the ex-  
30 cess raw material can be nitrated without delay, by spray-  
ing or foaming a dilute solution of acid to obtain intimate, overall  
contact with the fibre to a total moisture content of 30 to 50%, and  
held in storage in that form without being degraded by bacteria. Ex-  
tended periods of storage have been experienced up to one year in  
35 contact with the acid at a moisture level of 30-50% permitting usage of  
a very low percentage of acid to dry fibre, i.e. 1-3%.

The nitrated ligno-cellulosic material is next submerged in an alkali-



line, aqueous extraction solution, e.g. a solution of sodium, potassium, and/or ammonium hydroxide, so as to dissolve most of the nitrated lignin out of the fibrous structure. The lignin nitrate is substantially insoluble in acidic aqueous media, but is readily dissolved in basic aqueous media, for example having a pH of about 12.

The alkaline concentration of the extraction solution must be sufficient that the solution will leach out by dissolving most of the nitrated ligneous material in the fibrous structure. Usually it is preferred to use an alkaline strength (NaOH, KOH, or  $\text{NH}_4\text{OH}$ ) of preferably about 0.1 to 0.5 wt.%. If the nitration-extraction sequence is performed twice on the ligno-cellulosic material, then the alkaline strength used in the second extraction step need not be as high as that employed for the first extraction. Often the concentration of the alkaline solution used in the second nitration-extraction sequence will be about one-fifth to one-half that which is used in the initial sequence. The alkaline consumption is basically one of bringing the starting pH to about 12, and is therefore somewhat dependent on the concentration of residual acid remaining. The amount of the alkaline extraction solution used should be adequate to completely submerge the ligno-cellulosic material and dissolve most of the nitrated ligneous components. Usually the amount of alkaline extraction solution used will provide a slurry containing about 5 to 8 wt.% of the cellulosic fibre.

The temperature at which the alkaline extraction step is conducted should be sufficiently high to effect dissolution of most of the nitrated ligneous material. Preferably a temperature of about 75 to 100°C is used. Temperatures as low as 15°C can be used which will extend the time necessary for delignification. These low temperatures are particularly important in producing animal feed or partially defibered pulp from agricultural residues. Where straw as an example

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for an agricultural residue has been sprayed with nitric acid and held in storage, delignification with alkali under 50°C will produce  
5 a fully defibered pulp. The alkaline extraction step is best performed under atmospheric pressure conditions, thereby permitting the use of an open vessel and avoidance of expensive high pressure equipment. If desired, however, for example to further shorten the extraction time or utilize existing pressurized equipment, high temperatures and  
10 superatmospheric pressures, e.g. up to 10 or 15 p.s.i.g., can be used for the extraction. Increased time and temperatures using alkaline solutions will result normally in some degradation of the cellulose.

As discussed above with regard to the nitration step, the nitration -  
15 extraction sequence can be conducted just once, or it can be repeated, in which event each extraction step can be performed for a shorter period of time than if it were performed just once. It will be recognized that the time required to effect the desired degree of extraction is dependent on the particle size and type of the ligno-cellulosic material, and the temperature at which the extraction is conducted.  
20 In general, however, the total time required for the lignin-extraction, whether performed in one step or broken down into two extractions, will be no more than about 20 minutes, often being within the range of about 5 to 15 minutes .

25

If an open vessel is used for the extraction step, it can advantageously be a hydropulper. If a closed vessel is used, a screw conveyor may be preferred. After treatment with the alkaline extraction solution, the fibrous, cellulosic material is separated from the lignin-containing  
30 solution, preferably in a high density press. If, however, the fibre bundles are to be subjected to a second nitration-extraction sequence, then it will suffice to just drain off the extraction liquor. After the extraction step,  
35 the alkaline solution contains dissolved ligneous components and is reddish brown in colour. It is usually referred to as "black liquor". During start-up of the process all of the separated black liquor, together with the

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alkaline wash water, can be returned to the extraction vessel for reuse. As the process is continued, however, the content of dissolved solids in the black liquor will grow to a maximum tolerable concentration, e.g., somewhere in the range of about 10 to 25 wt.%, depending upon the quality of product desired. At that point an appropriate portion of the black liquor should be regularly removed and replaced with make up clear alkali liquor in order to prevent further increase in the concentration of the dissolved solids. The black liquor purge stream could be disposed of by various means such as by dumping as waste, or by concentrating and burning. Alternatively, the black liquor purge stream can be combined with the completely defibred pulp to supply ligneous binder for fiber web products prepared from the pulp, especially paperboard.

When the alkali lignin extraction process is complete the pH of the black liquor will be almost neutral, about 7.5 to 8.5 which is far lower than that of conventional alkaline processes the pH of which is usually in the range of 12-14. This factor of almost neutral pH makes the black liquor substantially more amenable to being handled in subsequent chemical processing. Sulphite acid systems produce black liquor in a pH range of 1.0 - 2.0.

Additionally, the black liquor has a very low range of BOD<sub>5</sub> (Biological Oxygen Demand - 5 day) and COD (Chemical Oxygen Demand) which together with its chemical make up permits its discharge in controlled amounts, up to 30%, in the normal urban effluent stream.

Typical comparative pollution data are as follows:

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	Values in mg/litre	Accelerated Pulping Black Liquor	Waste Paper Mill Effluent	Sulphite Mill Black Liquor
5		(From Spruce)		
	5 day biological oxygen demand	1500	8010	High
	Chemical oxygen demand	5685	16700	230,000
10	Permanganate number	11215	-	400,000

15 The BOD<sub>5</sub> value when related to recently recorded (North America) BOD<sub>5</sub> discharges per ton of pulp produced shows the following values: sulphite mill 109 kg; integrated sulphate pulp and paper mills 15 kg; waste paper mill 10 kg; and the accelerated pulping process: 30 kg. The low figure of the sulphate mill is reached only by burning all the black liquor solids produced to recover the major portion of the chemicals used in the process and the strict control of pollutants.

25 Although the black liquor could be discharged in a controlled manner into normal drainage facilities, it can be utilized uniquely and economically in a variety of ways as a binder, water repellent or size, extender for fortified rosin size, stiffening agent in paper board, fertilizer, hygroscopic additive to soil, extender for resins such as phenolics, and retention agent in papermaking. The solids in the black liquor are referred to as ligneous component. Although there are other chemical components than lignin and lignin nitrate, respectively, such as gums, waxes, etc. the lignin is the major component. Moreover, when precipitating the lignin, some of the said further components precipitate with the lignin. This is to be recognized when speaking of ligneous component.

The useful ligneous component can be precipitated from

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its mother black liquor by acidifying, preferably to a  
pH of 5.5 with any acid, but of particular usefulness are  
5 ordinary papermaker's alum (aluminum sulphate), recycled  
nitric acid from the process, and phosphoric acid.

For normal papermaking the black liquor precipitant (lige-  
ous component) resulting from acidification, e.g., with ni-  
10 tric acid or alum, can be added to the cellulosic pulp  
slurry, foamed (either in precipitated form or in form  
of the extraction liquor itself) and added at the wet pres-  
ses or size press, or can be added in its neutral pH form  
(black liquor) and acidified or not at the size press or  
15 wet presses. Unlike kraft liquor the black liquor under  
any normal treatment either in solution or precipitated  
exhibits the minimum and non-troublesome amount of foaming.  
The foaming of the black liquor, either itself or in con-  
centrated form (precipitated ligneous component) can be  
20 done by using a commercial surfactant or non-surfactant  
foaming chemical to foam water with air and then add as  
required the black liquor. This kind of application is  
known to the expert per se. However, not with the ligneous  
component.

25  
Addition of the precipitated black liquor (ligneous com-  
ponent) to the pulp slurry immediately lowers the stock  
freeness, i.e. drainage rate as it holds or retains the  
fine suspended particles usually lost through drainage on  
30 the paper machine wire.

Addition of the black liquor to paper, fibres in normal  
amounts up to 15% based on the solids and calculated on  
the dry weight of the fibre will increase the strength  
35 properties, i.e. burst strength and stiffness, in an approx-  
imate ratio of improvement of 1:1 to 2:1 for equal weight  
of cellulose fibre depending on the degree of openness of  
the fiber web making up the paper. When combined with

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the starch solution and added at high temperature (65°C or above) at the size press, a satisfactory sizing of the board (COBB 50) will be obtained, and the effectiveness of the starch on improving paper quality is greatly improved permitting reduced starch usage. A percentage of 0.4 to 0.6% of black liquor solids on the dry fibre content is sufficient.

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Addition in its neutral form (up to 60% solids) to a solution of 20% neutralized urea and 20% fortified rosin size will obtain sizing properties essentially equal to that of the rosin size when used alone. This combination can be precipitated on fibre suspensions in the conventional manner with alum. The neutral form of the black liquor precipitate is hygroscopic when dried and can be used when combined with fast draining materials such as sandy soils to retain moisture and chemicals. When the fibre cooking process and subsequent precipitation is formulated with all or part of those three chemicals essential to plant life, nitrogen (nitric acid), potassium (potassium hydroxide) phosphorus (phosphoric acid), the black liquor becomes a complete fertilizer in itself in addition to its retention properties. This can be readily achieved by using potassium hydroxide in the alkaline extraction step and by precipitating the ligneous component out of the extraction liquor by using phosphoric acid. Official government tests show normal germination and growth rates for barley and oats when this liquor is added to an inert clay. For easy handling, it can be combined with diatomaceous earth to inhibit hygroscopic properties.

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The acidified form of the black liquor, i.e. precipitant, can add its binding properties to such resins as melamine or phenolics permitting extension of these relatively expensive products. The neutral black liquor can be used in the preparation of resins since its nitrated form is com-

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patible chemically with that of many other resins. The acidified black liquor precipitant may be resolubilized by  
5 changing the pH to 7.5 with alkali and then again precipitated with acid at pH 5.5 making possible the concentration of the ligneous component through precipitation and then resolubilizing for further use in a neutral form.

10 During the alkaline extraction step most of the lignin nitrate dissolves in the alkaline solution, leaving the fibrous structure softened and partially defiberized. At this point the concentrated black liquor should be drained off for recycling or purging from the system as required. Since  
15 little mechanical and/or explosive force has been exerted the point of fibre liberation will not have been reached under normal pulping conditions. Some of the ligneous component remains partially around the fibres, holding them together, but defibering can be readily accomplished by  
20 appropriate mechanical means, for example, by subjecting the softened structure to the action of a double disc defibrator or a deflaking unit, machines which will physically break apart the soft fibre bundles without causing substantial injury to the fibres themselves.

25

It is preferable after mechanical defibering except for animal feed and semi-chemical type pulps to wash the fibres with water to remove surface alkali and black liquor. Washing is preferably accomplished with a minimal amount  
30 of hot water, e.g. at a temperature of about 85 to 100°C. The washing can be performed in any suitable manner. Following mechanical defibering and washing the cellulosic pulp can be subjected to a second nitration-extraction sequence, as discussed above, or it can be used in any of  
35 the conventional ways to make cellulosic fibre webs.

For pulps other than those intended for semi-chemical board or animal feed it will be necessary to screen the

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pulp, to remove any fibre bundles that withstood the pul-  
ping process, which bundles can then be returned to the  
5 nitration step or further defibering action.

Most commonly, the screened pulp will be supplied to the  
headbox of a paper machine, alone or in admixture with  
other types of fibres and there used to make paper pro-  
10 ducts.

In the previous text, substantial reference has been made  
to the processing of agricultural fibre residues, straw,  
bagasse into paper making fibres, using nitric acid as a  
15 nitrating agent, and aluminum sulphate (alum). It is a  
feature of this invention which sets it apart from all pre-  
vious experimentation with nitric acid, that in the case  
of fibrous structures, such as straw, that both nitration  
and delignification can be accomplished in one step using  
20 a solution of neutral nitrate salts such as  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$   
or  $\text{KNO}_3$  alkalized to a pH of about 11 to 12, e.g. 12, with  
 $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{NH}_4\text{OH}$  or other suitable alkali.

The ease of nitration in this case is dictated by the open  
25 structure of these fibrous materials, particularly so after  
shredding, coupled with the relative thin form of grassy  
fibrous structures compared to even 0.5mm thin wood flakes,  
their low lignin content of 10-15% vs. 25-35% for wood, and  
their low percentage of extraneous materials such as waxes  
30 and resins and other hydrophilic materials.

As previously stated, previous art using nitric acid, a  
highly aggressive agent, has employed high usage and con-  
centrations and lengthy time of treatment particularly for  
35 wood. The use of alum as an accelerator permits low con-  
sumption, low concentration and minimum processing time  
for woody fibrous structures in particular and grassy  
fibrous structures.

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The use of nitrate salts with their milder actions as opposed to the use of nitric acid plus alum is not practical for wood pulping and would not be economic for processing agricultural fibre residues, except for the possibility of combining the features of the process of this invention in providing controlled delignification, and the potential utilization of the black liquor as fertilizer, binder, sizing agent or resin extender.

The process of delignification serves to dissociate the fibres making up the natural fibre structure freeing the lignin and providing fibres which can be formed into a web for production of paper or board. On a modified or reduced scale of delignification in a relatively dry state ( 50% moisture) the lignin can be released in situ to act as a binder for the production of building board in which the fibrous structure remains essentially intact. Delignification will also increase the digestibility of fibrous structures by herbivores, cows and sheep etc. Animal feed is being produced commercially today from straw by addition of circa 5% NaOH to the dry weight of straw in a process which makes cubes or pellets with additional food additives. Additionally, work has been done with  $\text{NH}_4\text{OH}$ , liquid or gaseous  $\text{NH}_3$ , but this has not proven practical. Utilization of feed produced with NaOH is limited because the improvement in digestibility (food value) is low and the alkali content is high. An improvement to some 300% would be required to meet the food value of corn silage. Levels of improvement presently obtained processing straw are less than one tenth of this, and maximum utilization in the animals diet has not exceeded 15%.

This invention provides a controlled method of delignification which increases digestibility to the point that the processed straw can comprise a minimum of 50% of the animals total diet. Mixed during processing with other food

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supplements, molasses, dried milk, etc. a complete food can be formulated. Of equal importance is the potential of this process to be economic in small installations which further makes possible a joint production facility producing alternatively as required, animal feed and paper making fibre, providing flexibility to meet market demands local and long distance.

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It is characteristic of agricultural residues that they are bulky making it impossible to meet minimum weight requirements of shipping carriers resulting in high freight costs. Processing under this invention makes viable the production of a compact finished or semi-finished product of high density which greatly reduces freight and handling cost.

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The alternative provided by this invention in accomplishing nitration and subsequent delignification of agricultural residues extend to choices of acidic (nitric acid) or a variety of neutral nitrate salts in nitration, various levels of chemical concentration varying time and temperature for both nitration and delignification steps and a choice of alkaline chemicals (KOH, NaOH,  $\text{NH}_4\text{OH}$ ) to accomplish the pH level necessary for solution of the nitrated lignin.

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Consequently a variety of inexpensive mechanical installations for processing widely varied from present conventional pulping systems becomes not only possible but preferable. Schematic diagrams of two such possibilities are submitted as part of this invention. Figure 18, an ultra simple process involving a modified hydropulper for the production of pulp for paper which would provide an economic and viable unit for production levels as low as 10 tons per day. Figure 19 shows a completely flexible unit for the production of animal feed and for paper pulp uti-

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lizing hot air (which could be derived from burning agricultural residues) to achieve rapidly sufficient nitration  
5 temperatures (100°C) and the drying of the end product to a specific moisture level, as necessary.

The choice between the use of nitrate salts vs. nitric acid would be dictated by economics: (1) Twice as much salt  
10 would be necessary to achieve the same level of delignification as with nitric acid. (2) The reduced capital investment cost using salts since stainless steel would not be required for processing equipment. (3) The desired chemical content of the black liquor is provided, e.g.  
15 sodium ion built up in the soils if used for fertilizer would not be acceptable. (4) Differences in acceptability and digestibility by various animals digestive system or the chemical requirements required for further processing of the residual black liquor into sizing, binders or resin  
20 extenders.

The ability to spray or foam the nitrating liquid on dry agricultural residues makes possible a process that is essentially dry and permits the leaching out of the nitrated lignin after the alkaline liquor is added by  
25 spray or foam (an action that can follow immediately after the acid nitrating stage), when the moist mass (35-50% moisture) is subjected to heat and pressure. Enough lignin is released to provide a hardened binding material base  
30 sufficient to bind the shredded straw when subjected to an appropriate hardening agent such as alum and the usual pressures and temperatures used in the manufacture of flake board from wood residues. In this way an inexpensive building board, water resistant and stiff can be made from  
35 straw by generating its own binding materials eliminating the use of expensive resins such as phenolics.

The following examples are given as illustrations of the



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present invention; although it is not intended that they  
limit its scope in any way a wide variety of conditions  
5 and changes in variables is shown to illustrate the  
flexibility of the system.

Example 1

10 Southern pine wood flakes, cut tangentially to the log  
circumference to a thickness of about 0.6mm, are con-  
tinuously fed into a screw conveyor 10, as shown in  
Figure 1 attached hereto. The wood has a lignin content  
of about 35 wt.%. The flakes are submerged and cooked in  
15 about six times their weight of a solution of 5 wt.%  
nitric acid to which has been added aluminum sulphate in  
the ratio of 1 part aluminum sulphate to 10 parts  $\text{HNO}_3$   
for a period of about 15 minutes at a temperature of  
about 95°C. The slurry of flakes in acid is then fed into  
20 a spin 11 where the flakes are drained of the acid and  
then washed with a minimal amount of hot water. The  
drained excess acid and wash water are combined, fortified  
with alum and concentrated nitric acid as needed, and  
recycled for use in the initial nitration step. The flakes  
25 are then conducted to a storage vessel 12, from which they  
are fed into a screw conveyor 13 containing about six  
times their weight of a solution of about 1.5 wt.% sodium  
hydroxide at a temperature of about 95°C. There they are  
cooked for about 15 minutes. The flakes, partially de-  
30 fibered, are drained of the alkaline solution (in which  
the ligning-nitrate has dissolved) for its recycling or  
purging by a spin dryer 14; then are put through a de-  
fibrator 15 in order to separate the fibres partially,  
following which they are washed in a rotary washer 16  
35 with a minimal amount of hot water. The dilute black li-  
quor that is drained off in the spin dryer 14 is recycled  
to the first extraction step.

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In order to obtain a product with a higher degree of cellulose purity, i.e., bleachable pulp, not necessary for liner-board grade pulp, the nitration and digestion steps can be repeated. To do so, the semi-pulped flakes are fed into a screw conveyor 17 which contains about six times their weight of a solution of about 1.5 wt.% nitric acid to which aluminium sulphate has been added in the ratio of about 1 part to 10 parts  $\text{HNO}_3$ . There the semi-pulped flakes are cooked for a period of about 15 minutes at a temperature of about  $95^\circ\text{C}$ . The semi-pulp is then drained of excess acid and washed with a minimal amount of hot water in a spin dryer 18. The drain acid and wash water are combined and recycled to the second nitration step. The semi-pulp is then fed into a screw conveyor 19 which contains about six times its weight of a solution of about 0.8 wt.% sodium hydroxide. The semi-pulp is there cooked for about 10 minutes at a temperature of about  $95^\circ\text{C}$ . The semi-pulp is then drained of the excess alkaline solution (black liquor) in a high density press 20, after which it is fed into a defibrator 21 for additional defibering and finally washed in a rotary washer 22 with a minimal amount of hot water. The black liquor removed from the press 20 is partially recycled to the screw conveyor 19 for reuse, with the remaining portion being sent to waste disposal. The alkaline wash water from rotary washer 22 is also recycled to the second extraction step.

The pulp leaving the rotary washer 22 has been almost completely delignified and defiberized. It is then screened by conventional screening equipment 23 to remove oversized particles which have not been defiberized, which are returned to the nitration step for reprocessing.

#### Examples 2 - 7

The process of Example 1 is repeated, using different

ligno-cellulosic raw materials, as indicated in the following Table III.

In each example the nitric acid contains 1 part aluminum sulphate for each 10 parts of  $\text{HNO}_3$ . The same applies for examples 8 through 14.

In examples 4 through 7 the ligno-cellulosic material is subjected to only one nitration-extraction sequence.

Example 8

This example simulates the use of a sulphite digester producing bleachable pulp (Kappa No. 8) using pressure under conditions as follows: -

	WOOD	SPRUCE
	FORM	FLAKES 0.5-0.6mm thick
	CHARGE	1.3kg (DRY)
20	DIGESTER	STATIONARY CIRCULATING
	IMPREGNATION TIME	15 MINUTES
	IMPREGNATION TEMPERATURE	70°C
	IMPREGNATION CHEMICAL CON- CENTRATION	5% $\text{HNO}_3$
	COOKING TIME	15 MINUTES
	TIME TO COOKING TEMPERATURE	2 MINUTES
25	COOKING TEMPERATURE	85-95°C
	COOKING CHEMICAL	7.5% $\text{HNO}_3$
	RATIO LIQUOR TO DRY WOOD	4:1
	PRESSURE	7-22 P.S.I.G.
	GAS OFF	NONE
	DELIGNIFICATION STAGE	20 MINUTES
	DELIGNIFICATION TEMPERATURE	95-100°C
30	DELIGNIFICATION CHEMICAL	0.25% NaOH
	DELIGNIFICATION PH	10.0 - 8.0

Test results on the paper produced were as follows: -

		<u>First Sequence</u>				<u>Second Sequence</u>				<u>Approximate Total</u>	
		<u>Nitric Acid</u>		<u>Sodium Hydroxide</u>		<u>Nitric Acid</u>		<u>Sodium Hydroxide</u>	<u>Chemical Usage,</u>		
									<u>Wt.% of Fibre Used</u>		
Example	Ligno-Cellulosic Fibrous Material										
2 Spruce (Norway) (0.5mm flakes)	33	4.4	4:1	0.3	5:1"	1.5	8:1	0.1	20:1	5.0	2.0
3 Beech (0.8mm flakes)	23	3.2	4:1	0.3	5:1	1.1	8:1	0.1	20:1	4.5	2.0
4 Bagasse (screened)	19	1.5	7:1	0.2	20:1	-	-	-	-	4.0	1.8
5 Straw (shredded)	16	1.5	10:1	0.1	20:1	-	-	-	-	4.0	1.8
6 Newsprint waste (pulped)	25	1.0	15:1	0.2	20:1	-	-	-	-	8.0	3.0
7 Bamboo (flaked)	24	3.0	5:1	0.2	20:1	-	-	-	-	4.0	1.8

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	REFINING-MINUTES	0	5	7	10	13
	<u>TEST</u>					
5	FREENESS, °SR	21	27	39	46	52
	BASIS WEIGHT, GR/M <sup>2</sup>	81.7	80.9	78.5	80.0	80.9
	CALIPER, MM	0.115	0.100	0.094	0.089	0.089
	APPARENT DENSITY, KG/MM <sup>3</sup>	0.710	0.809	0.835	0.899	0.909
	ELONGATION, %	1.9	2.9	2.8	2.7	3.2
10	TENSILE STRENGTH, MTR	6660	7400	7360	7480	8240
	MULLEN ABS, KPG	258	360	324	312	380
	MULLEN INDEX, KPA	316	444	412	390	470
	TEAR-BRECHT IMSET, MN	1118	1187	942	922	1109

15 Example 9

A non-pressure process using low concentration circulated chemical and longer times producing linerboard pulp, Kappa No. 37 used the following conditions: -

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	WOOD	SPRUCE FLAKES, 0.5-0.6mm
	CHARGE	1.3 KG., DRY
	IMPREGNATION TIME	30 MINUTES
	IMPREGNATION TEMPERATURE	50°C
	IMPREGNATION CHEMICAL	0.5% HNO <sub>3</sub> SOLUTION
	COOKING TIME	45 MINUTES
25	COOKING TEMPERATURE	95°C
	COOKING CHEMICAL	1.8% HNO <sub>3</sub> SOLUTION
	DELIGNIFICATION	NaOH, pH 12, 95°C

Example 10

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A non-pressure process using a hydropulper producing a bleachable straw pulp Kappa No. 16.

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	WHEAT STRAW	MECHANICALLY SHREDDED
	CHARGE	1.2 KG., DRY
	IMPREGNATION TIME	15 MINUTES
5	IMPREGNATION TEMPERATURE	50°C
	IMPREGNATION CHEMICAL	0.5% HNO <sub>3</sub> SOLUTION
	COOKING TIME	15 MINUTES
	COOKING TEMPERATURE	95°C
	COOKING CHEMICAL	1.5% HNO <sub>3</sub> SOLUTION
	DELIGNIFICATION	NaOH, pH 12, 95°C

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Example 11

A non-pressure process using a hydrapulper producing an animal feed grade of straw: -

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	WHEAT STRAW	MECHANICALLY SHREDDED
	CHARGE	1.2KG., DRY
	IMPREGNATION TIME	15 MINUTES
	IMPREGNATION TEMPERATURE	50°C
	IMPREGNATION CHEMICAL	0.05% HNO <sub>3</sub> SOLUTION
	COOKING TIME	15 MINUTES
	COOKING TEMPERATURE	95°C
20	COOKING CHEMICAL	0.15% HNO <sub>3</sub> SOLUTION
	DELIGNIFICATION	NaOH, pH 12, 95°C

Example 12

25 A spray storage system for straw to produce pulp for packaging papers:

	WHEAT STRAW	MECHANICALLY SHREDDED
	STARTING MOISTURE	12% (BEFORE SPRAYING)
	FINISHING MOISTURE	35%
30	CHEMICAL SPRAYED	3% HNO <sub>3</sub> (100%) OF DRY FIBRE WEIGHT
	HEAT APPLIED	NONE
	STORAGE PERIOD	SIX MONTHS
	DELIGNIFICATION	NaOH, pH 12
	DELIGNIFICATION TIME	10 MINUTES
	DELIGNIFICATION TEMPERATURE	50°C

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Example 13

A non-pressure process using an open hydrapulper producing a semi-chemical type pulp for use as corrugating medium

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combined with waste fibre and straw black liquor (lignin) solids.

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	WHEAT STRAW	MECHANICALLY SHREDDED
	CHARGE	1.2 KG ATRO
	IMPREGNATION TIME	15 MINUTES
	IMPREGNATION CHEMICAL	0.05% $\text{HNO}_3$ CONC.
	IMPREGNATION TEMPERATURE	50°C
	COOKING TIME	30 MINUTES
10	COOKING CHEMICAL	0.15% $\text{HNO}_3$ CONC.
	COOKING TEMPERATURE	95°C
	DELIGNIFICATION	15 MINUTES, NaOH to pH 12-95°C

#### Board Composition

	<u>%</u>
15 DEFIBERED UNSCREENED PULP	42
MIXED WASTE FIBER	33
UNMODIFIED LIGNIN SOLIDS	25

#### Test Results - Produced on Paper Machine

20 BASIS WEIGHT, GR/M <sup>2</sup>	105
MULLEN INDEX, KPA	233
ELMENDORF TEAR, MD/CD-MN	677/716
25 CONCOR, KG P	158

#### Example 14

30 A non-pressure process using an open hydropulper producing a bleachable straw pulp.

	WHEAT STRAW	MECHANICALLY SHREDDED
	CHARGE	1.2 KG ATRO
	IMPREGNATION TIME	15 MINUTES
	IMPREGNATION CHEMICAL	0.5% $\text{HNO}_3$ CONC.
	IMPREGNATION TEMPERATURE	50°C
	COOKING TIME	15 MINUTES
35 COOKING CHEMICAL	1.5% $\text{HNO}_3$ CONC.	
	COOKING TEMPERATURE	95°C
	DELIGNIFICATION	15 MINUTES, NaOH to pH 12-95°C

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Test Results - Produced on Paper Machine

5	BASIS WEIGHT, GR/M <sup>2</sup>	180
	MULLEN INDEX, KPA	495
	ELMENDORF TEAR, MD/CD-MN	739/848
	SCHOPPER RIEGLER, DEGREES	50
	KAPPA, NO.	16

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Example 15

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A non-pressure neutral pH-cooking process using an open hydropulper producing a packaging paper pulp.

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BAGASSE	SCREENED - DEPITHED
COOKING TIME	15 MINUTES
COOKING CHEMICAL	NaNO <sub>3</sub> - 3% SOLUTION
COOKING TEMPERATURE	95 - 100°C
DELIGNIFICATION	15 MINUTES, NaOH to pH 12, 95°C

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Electron micrographs of illustrative cellulosic fibres produced by the process of the present invention are shown in Figures 2 through 17. In each instance sodium hydroxide was used as the alkaline extraction agent and both the

25 nitration step and the extraction step were conducted at temperatures within the range of about 95 to 100°C at atmospheric pressure. Final defibering was performed by two minutes in a blender; then the pulp was submitted to rough screening. The excellent length and structure of the fibres

30 are apparent from the micrographs.

Figures 2 and 3 are electron micrographs of fibres from U.S. Southern pine which had been subjected to a total nitration-extraction time (total for both steps) of 25

35 minutes, while Figures 4 and 5 show such pine fibres after only a 20 minute nitration-extraction time. Figures 6 and 7 are micrographs of fibres of spruce which had been subjected to a nitration-extraction time of 25 minutes. Figures



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10 and 11 show wheat straw fibres after a nitration-  
extraction time of 25 minutes. Figures 12 and 13 are micro-  
5 graphs of beech fibres obtained from the present process  
using a combined nitration-extraction time of 27.5 minutes.  
Figures 14 and 15 are micrographs of bamboo fibres which  
had been subjected to a nitration-extraction time of 30  
minutes. Figure 16 is a micrograph of fibres obtained  
10 from waste newspapers which had been subjected to a  
nitration-extraction time of 15 minutes. Figure 17 shows  
fibres from old U.S. corrugated paperboard which had been  
subjected to a nitration-extraction time of 15 minutes.

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DOST & ALTENBURG

PATENTANWALTE

0012775

WOLFGANG DOST, DR. RER. NAT. DIPL.  
UDO ALTENBURG, DIPL.-PHYS.

8 MÜNCHEN 80 GALILEIPLATZ  
TELEFON: 089-98860  
TELEGRAMME: GALILEI 27 MÜNCH.  
TELEX: 05-2279. D-11

DATUM: December 20, 19  
P 1304 D/Kr

C l a i m s

- 1 1. A process for treating fibrous ligno-cellulosic material  
to form defibered pulp material comprising the steps of  
submerging in or spraying of the fibrous ligno-cellulosic  
material with aqueous nitric acid having an  $\text{HNO}_3$  concen-  
5 tration of about 0.15 to 9.0 wt.% and containing aluminum  
sulphate in an amount of about 0.8 to 1.3 parts per each 10  
parts by weight of  $\text{HNO}_3$ , or to alternatively use for grassy  
fibrous materials nitrate salts such as  $\text{NaNO}_3$  or  $\text{KNO}_3$  or  
 $\text{NH}_4\text{NO}_3$ , so as to nitrate ligneous component of said material  
10 draining, the nitrated ligno-cellulosic material from said  
nitric acid and thereafter defiberizing directly by mechan-  
ical means to obtain said pulp material, or treating the  
said nitrated ligno-cellulosic material with an alkaline  
extraction liquor so as to dissolve ligneous component out  
15 of the material and separating the resultant cellulosic pulp  
from the lignin containing extraction liquor as well as,  
optionally, recombining a part or all of the ligneous com-

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ponent of the lignin containing extraction liquor with the cellulosic pulp.

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2. The process of claim 1 wherein the fibrous ligno-cellulosic material is submerged in or treated by recycling in nitrating solution at a temperature of about 85 to 110°C, preferably 85 to 100°C; in particular wherein both the  
10 submersion step and the cooking step are conducted under approximately atmospheric pressure conditions and the  $\text{HNO}_3$  concentration in the nitrating step is about 0.3 to 5.5 percent by weight; in particular wherein the fibrous ligno-cellulosic material is submerged or subjected to treatment  
15 by recycling in the nitrating solution for about 5 to 30 minutes; in particular wherein the ligno-cellulosic material is woody material, grassy material, or waste paper containing mechanical pulp or semi-chemical fibres; in particular wherein the submersion step and the cooking  
20 step are conducted under atmospheric pressure conditions and the fibrous ligno-cellulosic material is submerged in or treated by the nitrating solution for about 10 to 20 minutes; in particular wherein pressures of 15 to 35 p.s.i.g. are used in the nitrating process holding temperatures from 85 to 110°C, preferably 85 to 100°C; in particular wherein  
25 pressures of 100 to 150 p.s.i.g. are used in the nitrating process holding temperatures between 85 and 110°C, preferably 85 and 100°C.

3. The process of claim 1 or 2, wherein the alkaline  
30 extraction liquor is an aqueous solution of sodium hydroxide, potassium hydroxide, or ammonium hydroxide containing about 0.1 to 0.5 wt.% NaOH, KOH or  $\text{NH}_4\text{OH}$ ; in particular wherein the alkaline extraction liquor is an aqueous solution of sodium hydroxide containing about 0.1 to 0.5 wt.%  
35 NaOH, the fibrous ligno-cellulosic material is submerged in the nitrating solution at a temperature of about 90 to 95°C and the nitrated ligno-cellulosic material has its binding material removed; in particular wherein the alkali-

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ne extraction liquor is an aqueous solution of potassium  
hydroxide, the lignin containing extraction liquor is  
5 mixed with phosphoric acid to precipitate the ligneous  
component out of the solution and the ligneous component  
is separated from its acidic mother liquor to obtain a  
flocculated concentrated ligneous material; in particular  
wherein the nitrated ligno-cellulosic material is treated  
10 in the alkaline extraction liquor at a temperature of  
about 75 to 100°C for grassy and woody fibrous structures;  
in particular wherein the nitrated ligno-cellulosic ma-  
terial is treated in the alkaline extraction liquor of  
about 40 to 50°C for grassy fibrous structures.

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4. The process of any of the preceeding claims wherein the  
ligneous component is obtained by mixing the lignin con-  
taining extraction liquor with acidic reagent to cause  
ligneous component to precipitate out of solution, follo-  
20 wing which said precipitated ligneous component is separa-  
ted from its acidic mother liquor; in particular wherein  
the acidic reagent is nitric acid, phosphoric acid or alu-  
minum sulphate; in particular wherein the acidic reagent  
is nitric acid and the acidic mother liquor is used as a  
25 source of nitric acid for the precipitation step; in parti-  
cular wherein the precipitated ligneous component prior to  
be mixed with the cellulosic pulp, is redissolved in water  
with sufficient alkaline reagent to render the ligneous  
component soluble in water; in particular wherein the  
30 alkaline reagent is sodium hydroxide, potassium hydroxide  
or ammonium hydroxide; in particular wherein the floccula-  
ted concentrated ligneous material, optionally in combina-  
tion with a deliquescence inhibiting amount of diatoma-  
ceous earth is added to quick draining soils to promote  
35 chemical retention and hygroscopic properties.

5. The process of any of the preceeding claims wherein the  
lignin containing extraction liquor or the redissolved

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ligneous component is combined with neutralized urea and fortified rosin size to extend rosin size; in particular  
5 wherein the lignin-containing extraction liquor or the precipitated ligneous component or the redissolved ligneous component is combined with starch to produce water repellency or sizing; in particular wherein the lignin-containing extraction liquor or the redissolved ligneous component is  
10 mixed with resins such as melamine resin or phenolic resin to act as an extender; in particular wherein the nitrated lignin can be solubilized with an alkaline solution at low temperatures of 15 to 50°C.

15 6. The process of any of the preceeding claims wherein the separated ligneous component is combined in precipitated (concentrated) or non-precipitated form with papermaking fibre.

20 7. The process of any of the preceeding claims wherein the recombination of the ligneous component with said cellulosic pulp is performed by applying a foam of the precipitated or non-precipitated ligneous component onto a web of the cellulosic pulp at the size press or wet  
25 presses; in particular wherein the recombination of the ligneous component with said cellulosic pulp is performed by adding the lignin-containing extraction liquor to the slurry of the cellulosic pulp and precipitating the ligneous component by acidification.

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8. The process of any of the preceeding claims wherein the nitrating solution can be sprayed on air dry grassy agricultural residues and nitrates the said residue lignin components during storage without use of heat permitting

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delignification and defibering at a later date; in particular wherein the nitrating solution can be sprayed or  
5 foamed on air dry agricultural residues and followed immediately with sprayed or foamed alkaline liquor which releases a ligneous binder "in situ" when the moist mass is subjected to heat and pressure.

10 9. The process of any of the preceeding claims wherein the digestibility of agricultural residues for animals is improved.

10. A fertilizer composition comprising the ligneous material of claim 4 in a mixture with a deliquescence inhibiting  
15 amount of diatomaceous earth.

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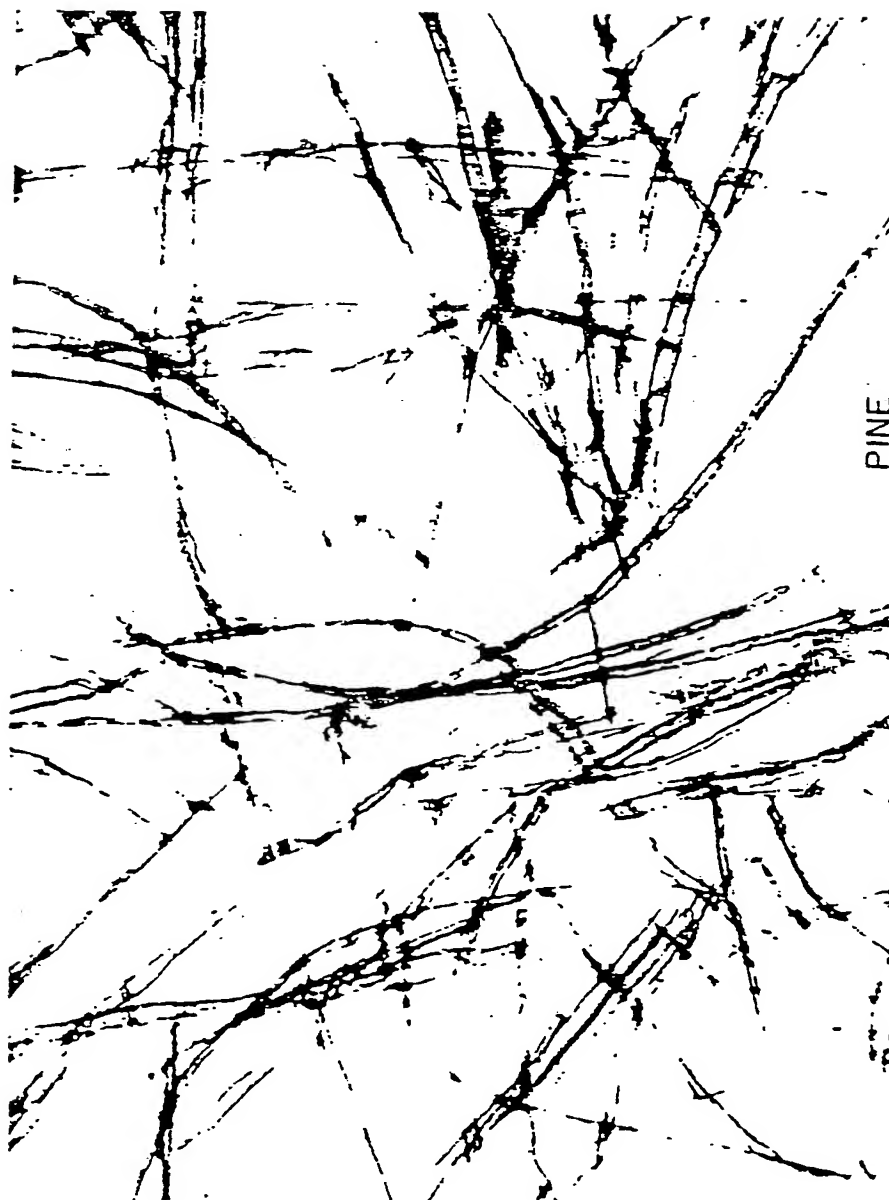
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graph TD
    10[10 FIRST NITRATION] --> 11[11 DRAIN AND WASH]
    11 --> 12[/12 STORAGE/]
    12 --> 13[13 FIRST EXTRACTION]
    13 --> 14[14 DRAIN]
    14 --> 15[15 DEFIBRATOR]
    15 --> 16[16 WASH]
    16 --> 17[17 SECOND NITRATION]
    17 --> 18[18 DRAIN AND WASH]
    18 --> 19[19 SECOND EXTRACTION]
    19 --> 20[20 PRESS]
    20 --> 21[21 DEFIBRATOR]
    21 --> 22[22 WASH]
    22 --> 23[23 SCREEN]
    23 --> PM[TO PAPER MACHINE]
    23 --> NP[OVERSIZE PARTICLES TO NITRATION]
    
    10 --> 11
    11 --> 12
    12 --> 13
    13 --> 14
    14 --> 15
    15 --> 16
    16 --> 17
    17 --> 18
    18 --> 19
    19 --> 20
    20 --> 21
    21 --> 22
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```

FIG. 2



PINE

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FIG. 3

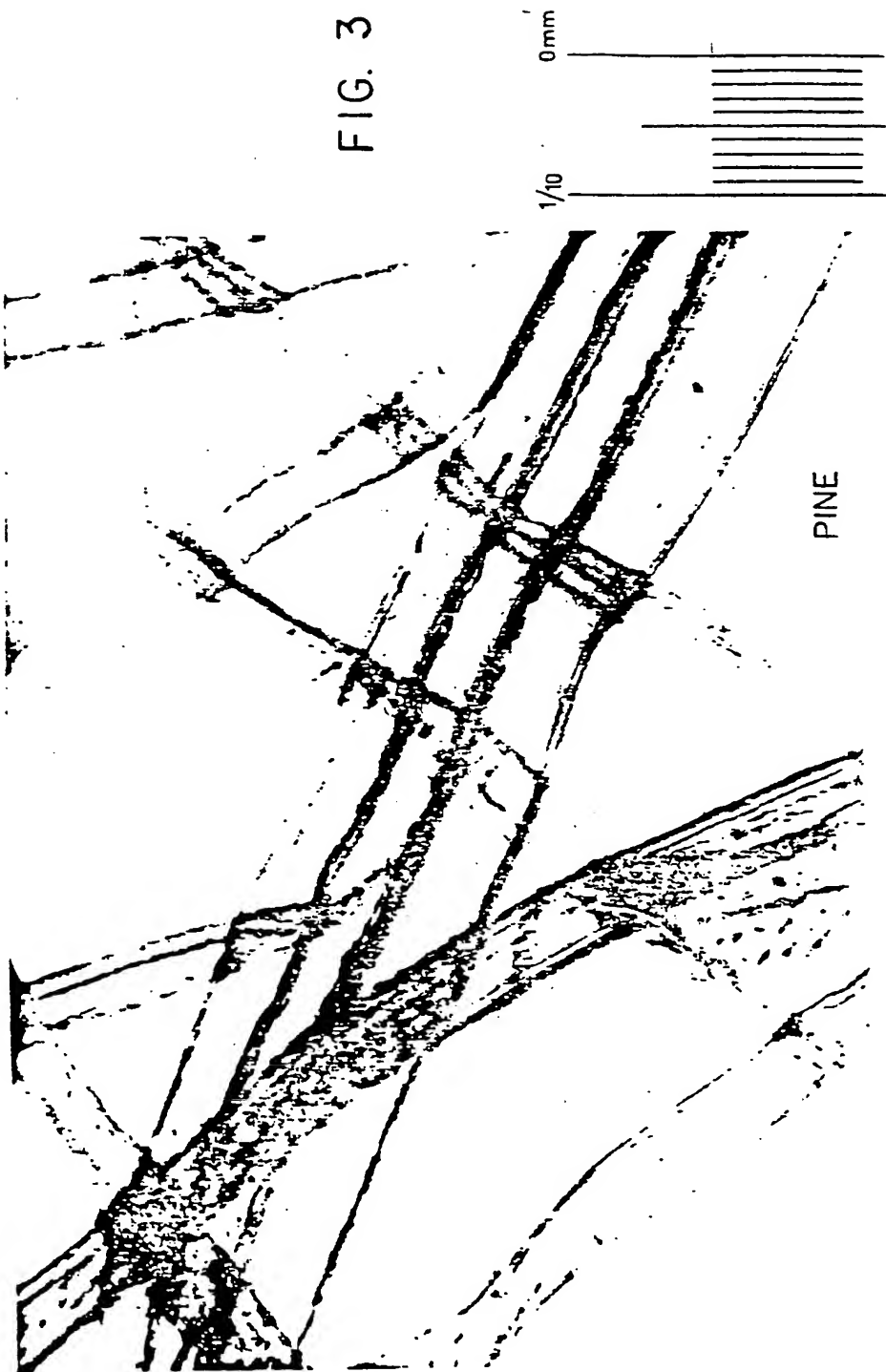


FIG. 4



FIG. 5

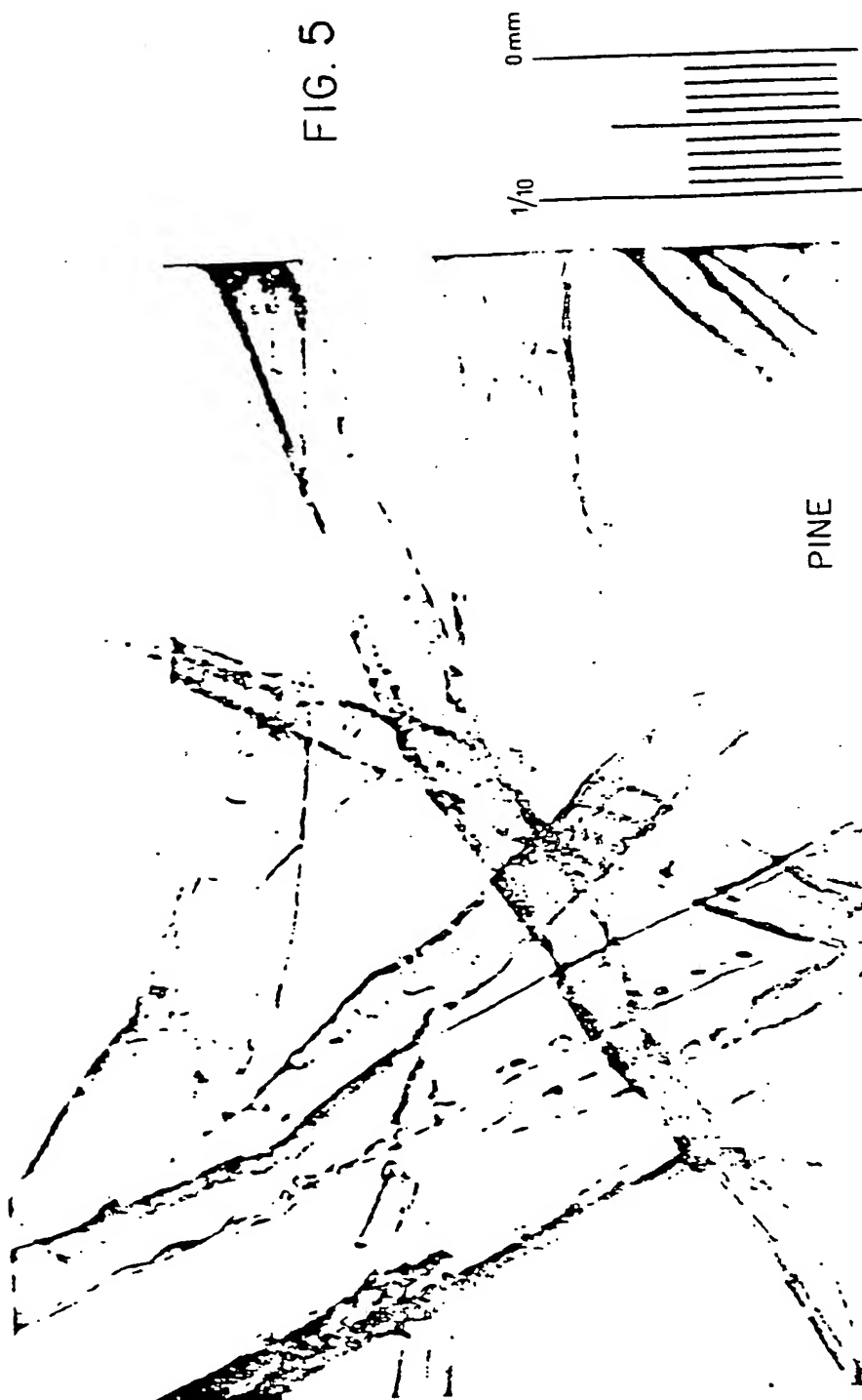
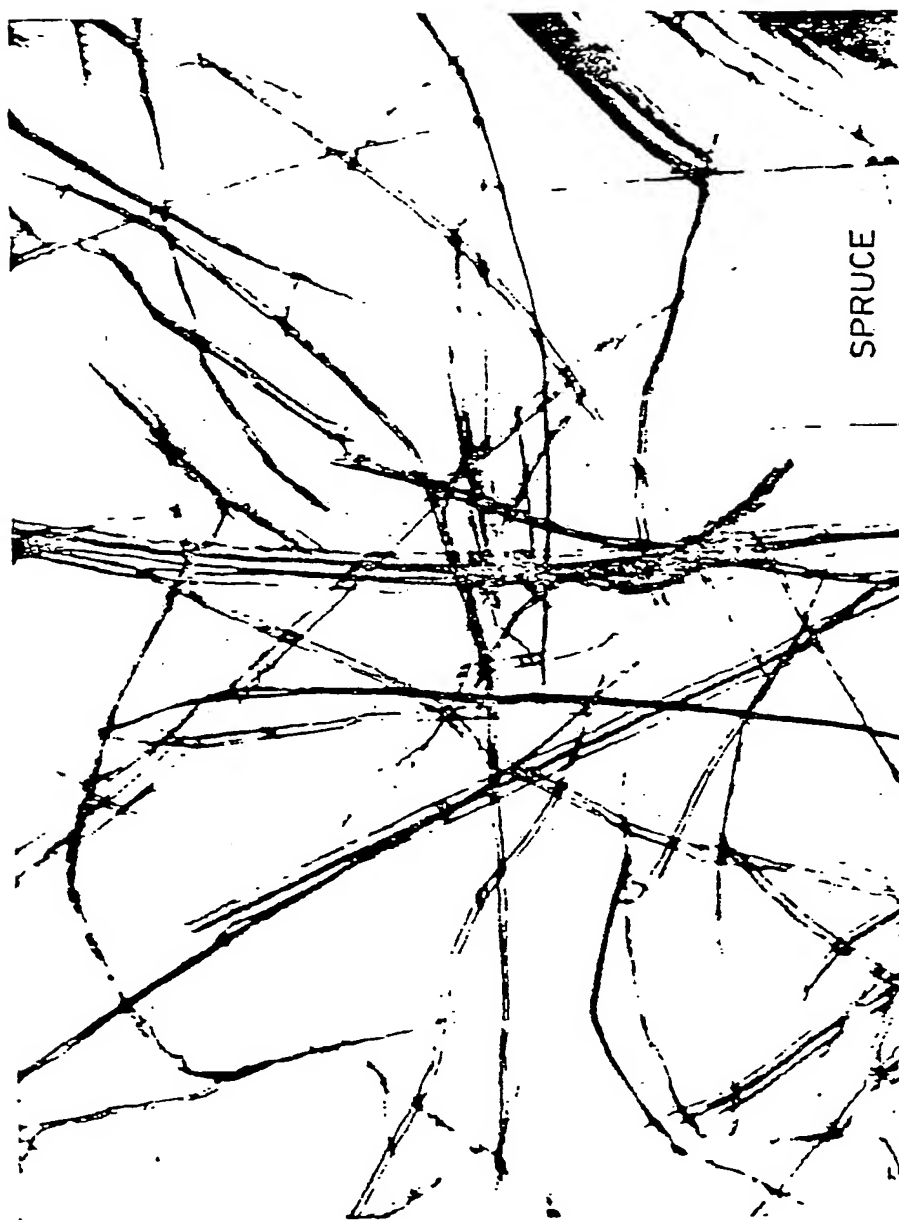


FIG. 6



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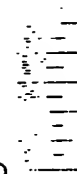


FIG. 7

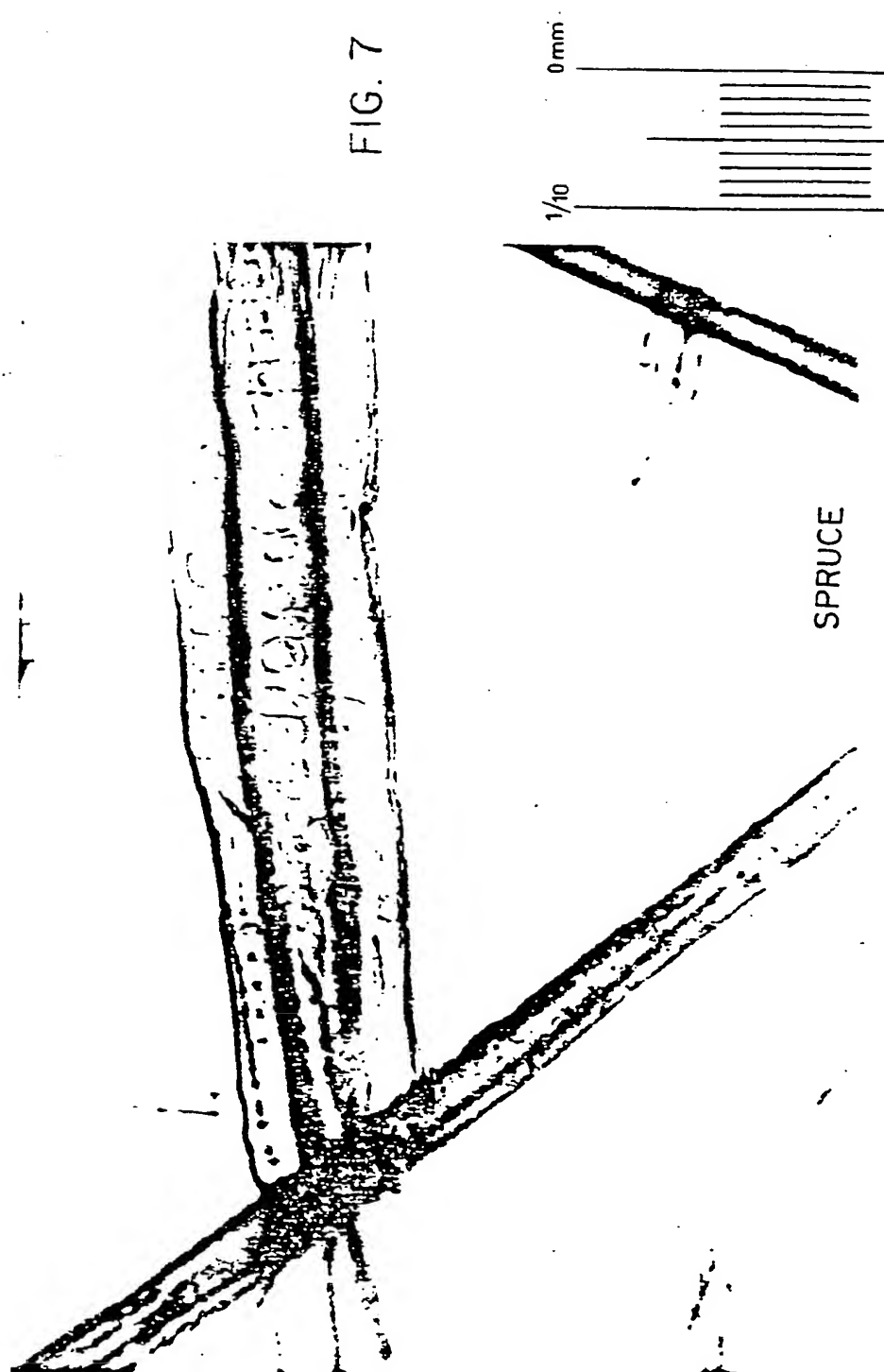
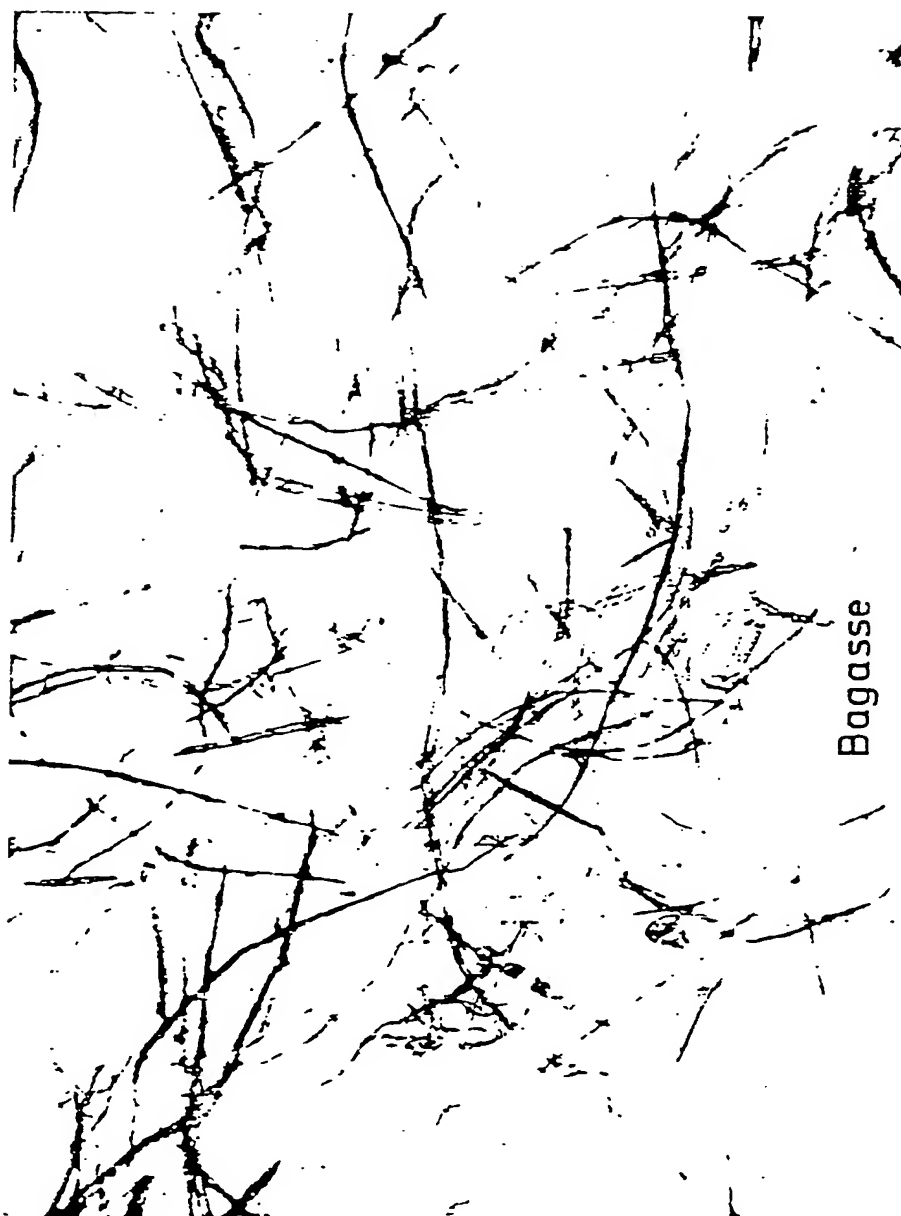


FIG. 8



Bagasse

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FIG. 9

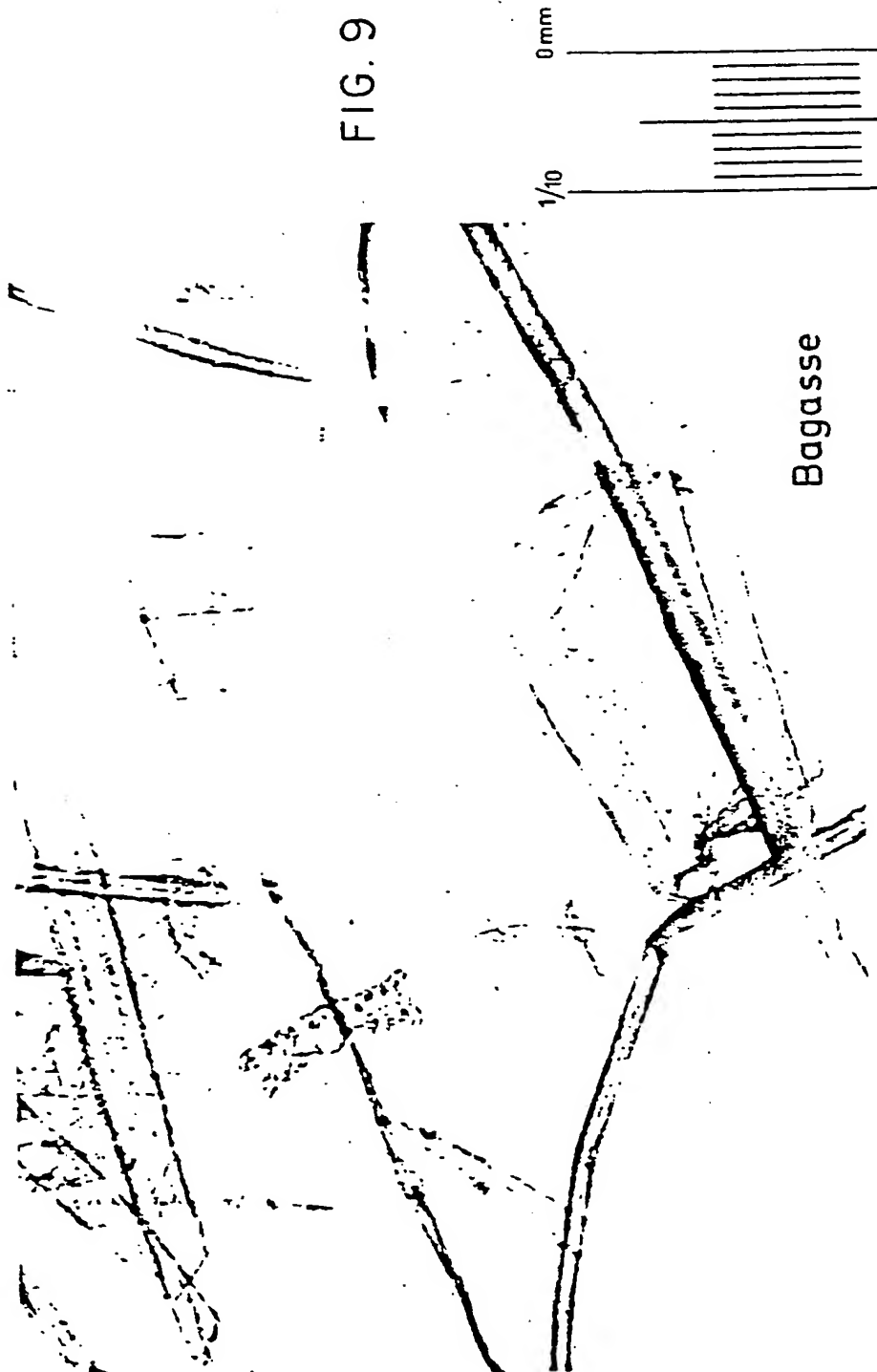
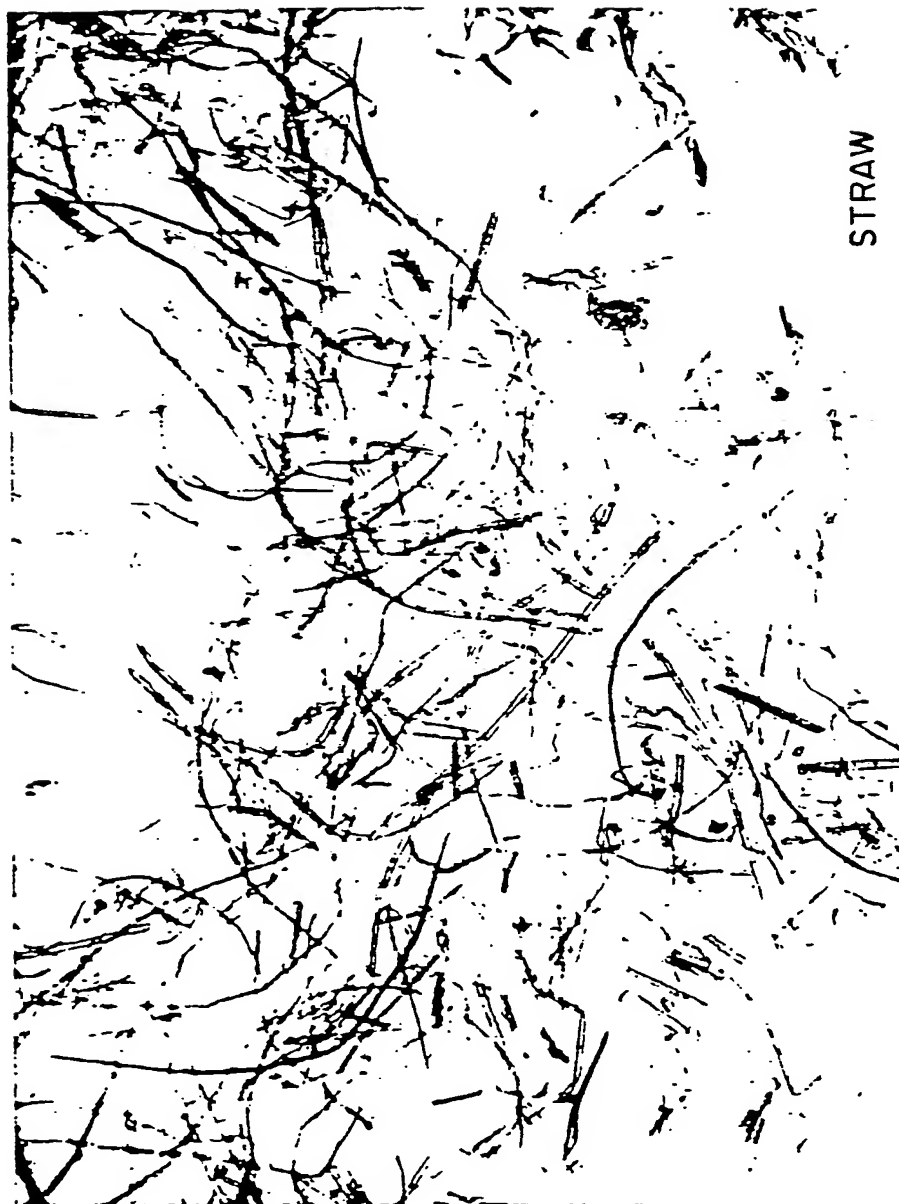


FIG. 10



STRAW

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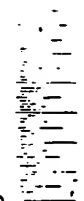




FIG. II

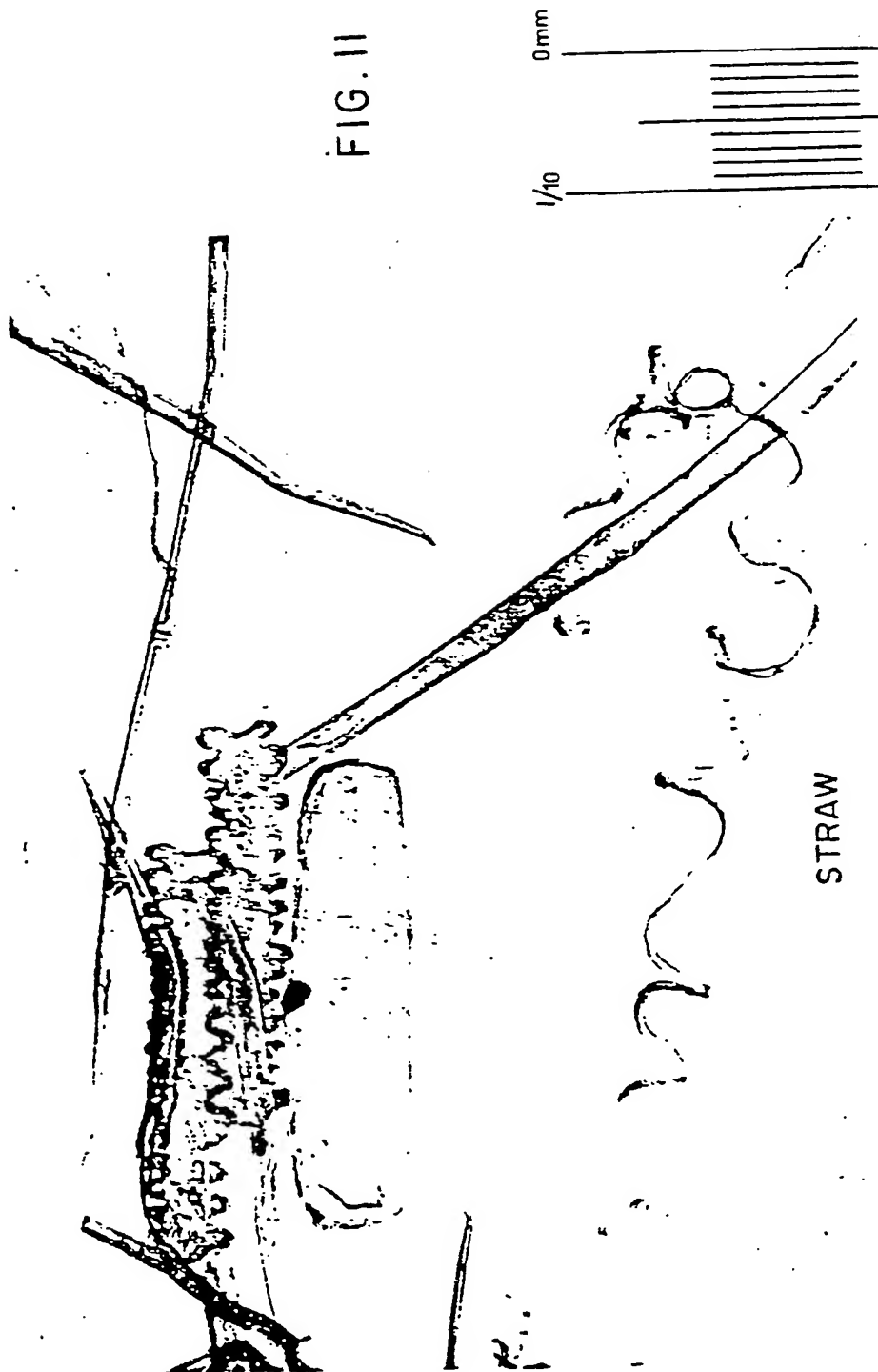
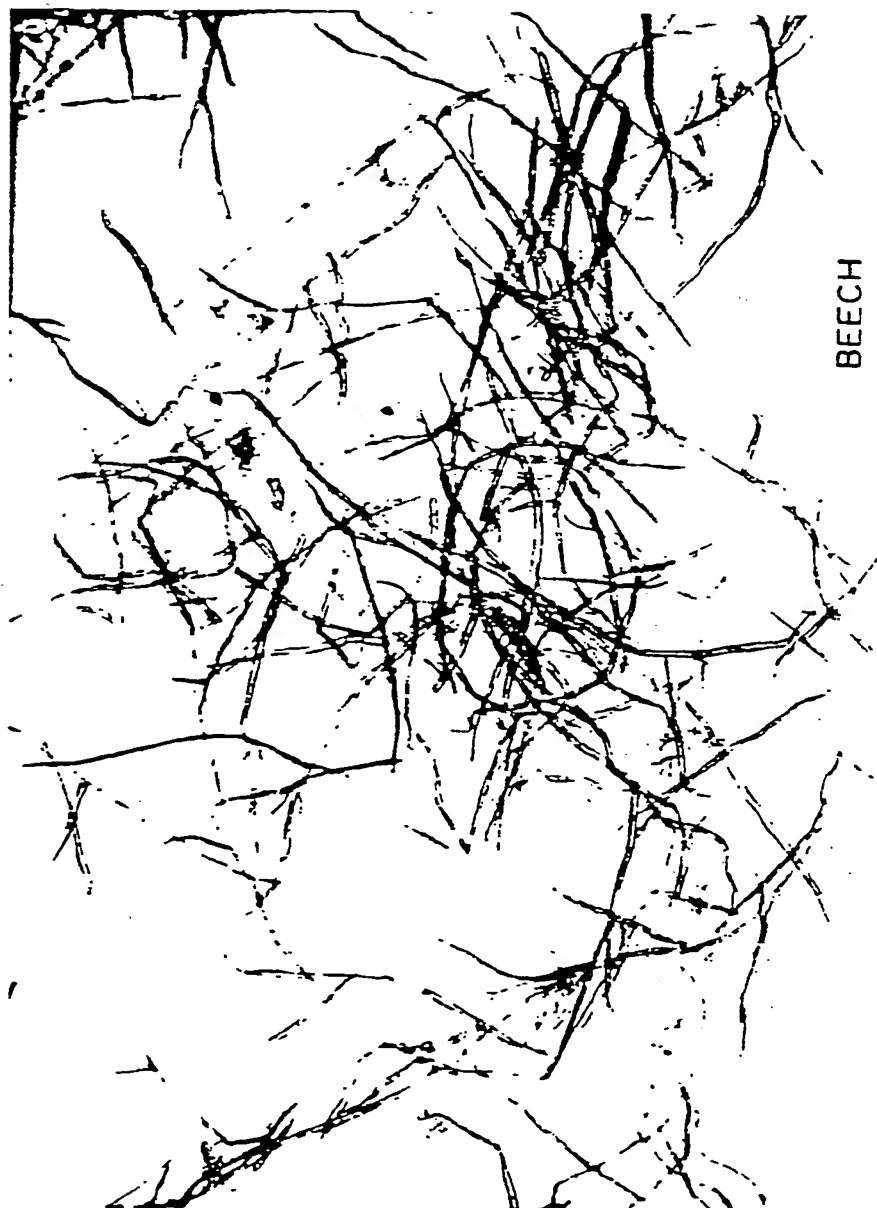


FIG. 12



BEECH

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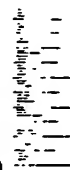


FIG. 13

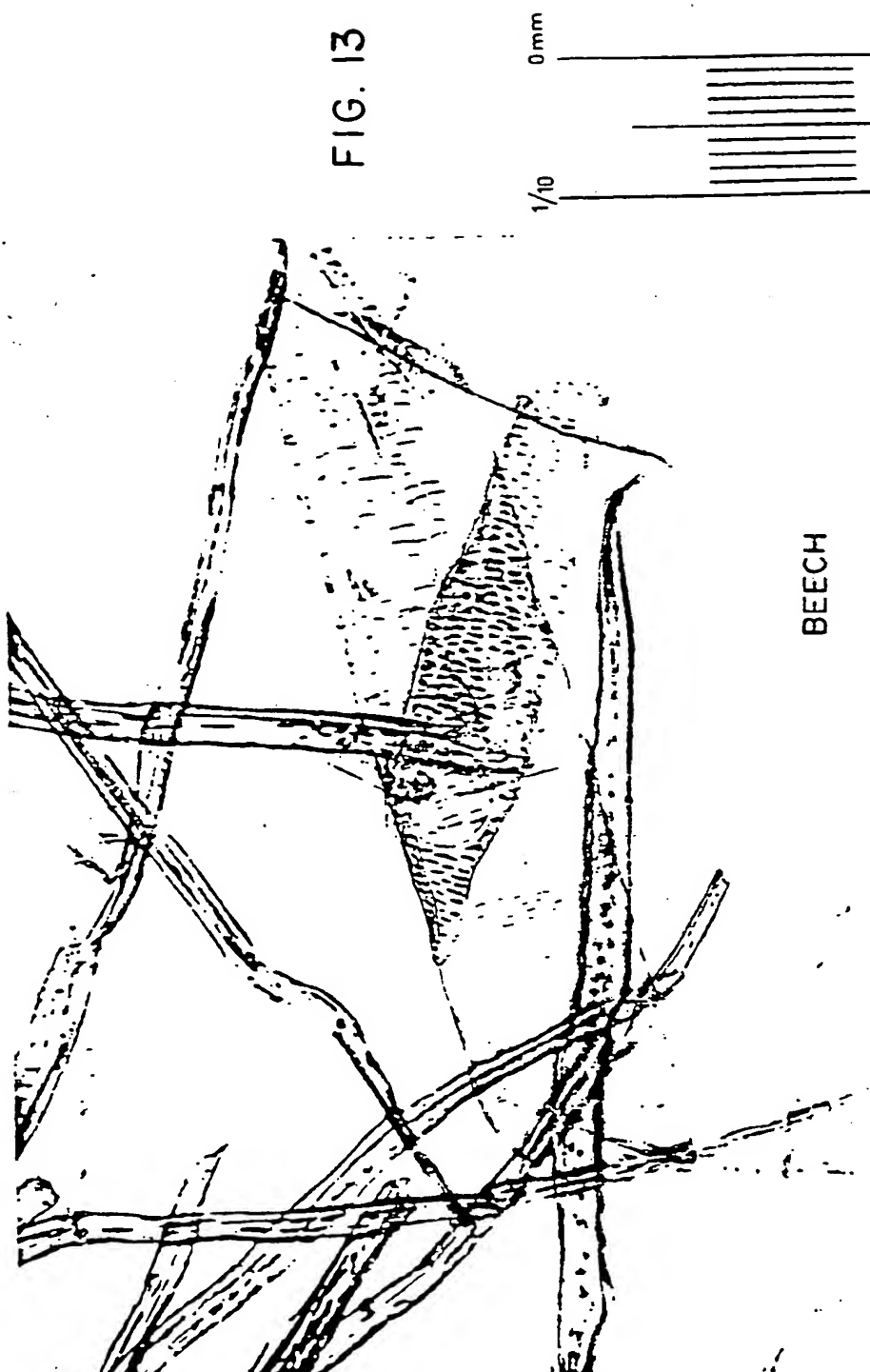


FIG. 14

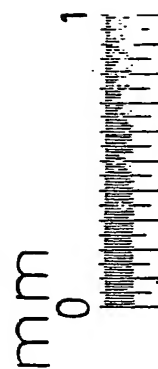
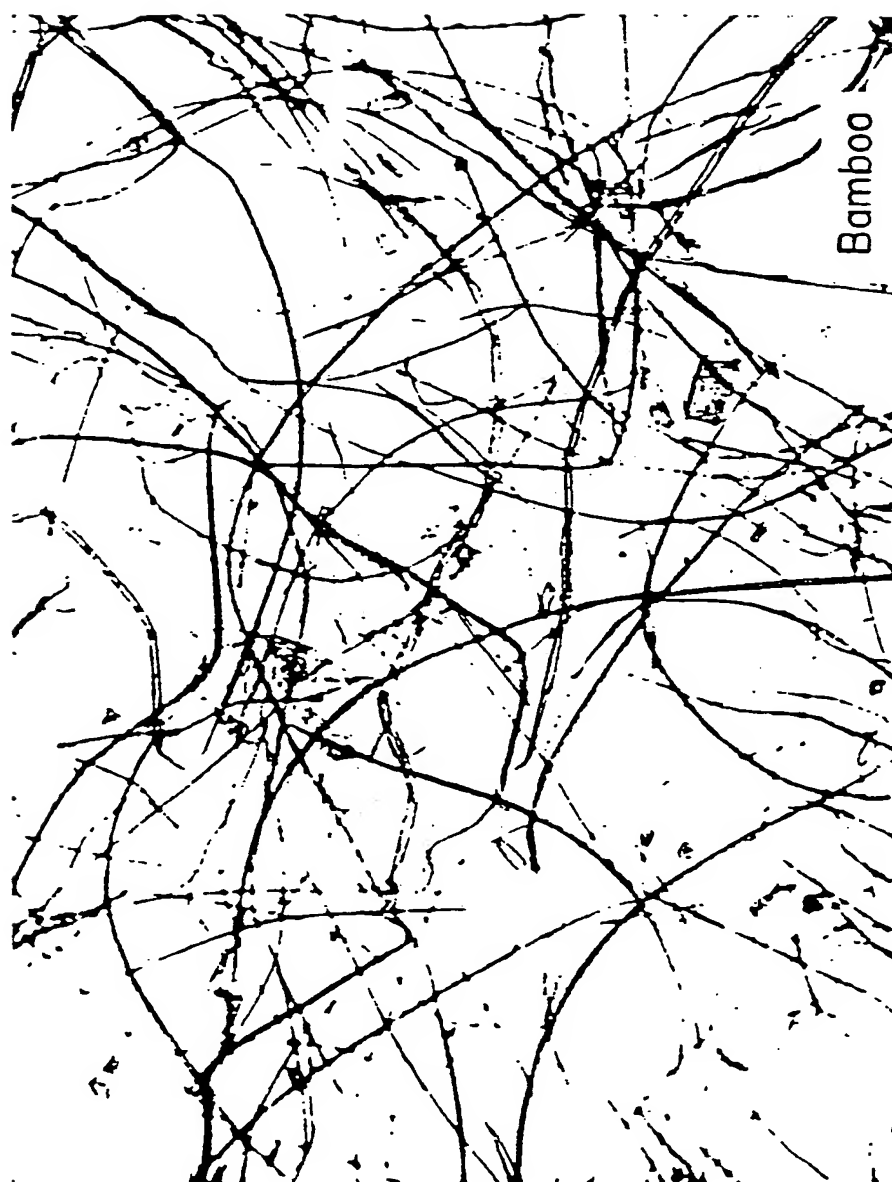
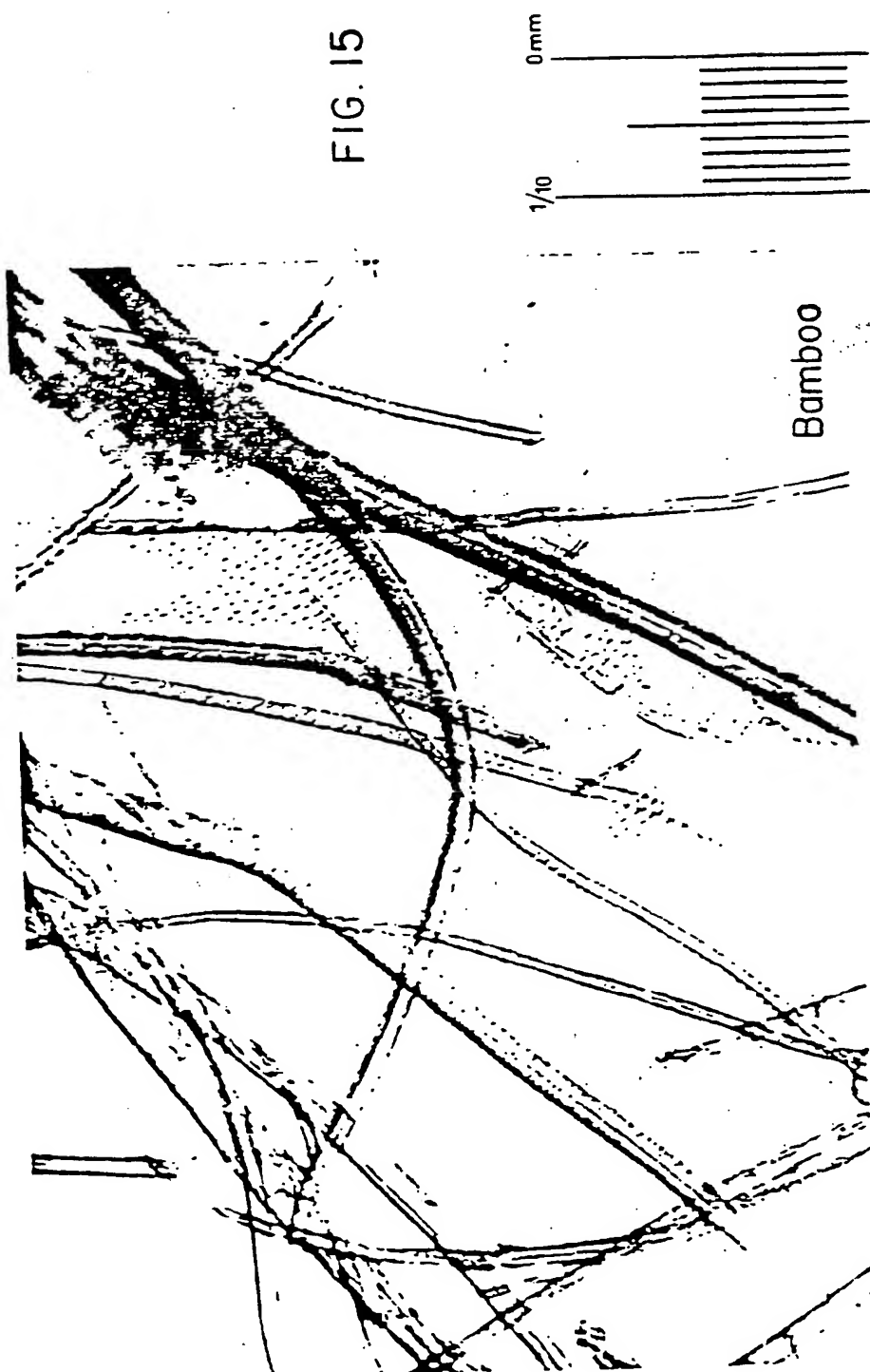


FIG. 15

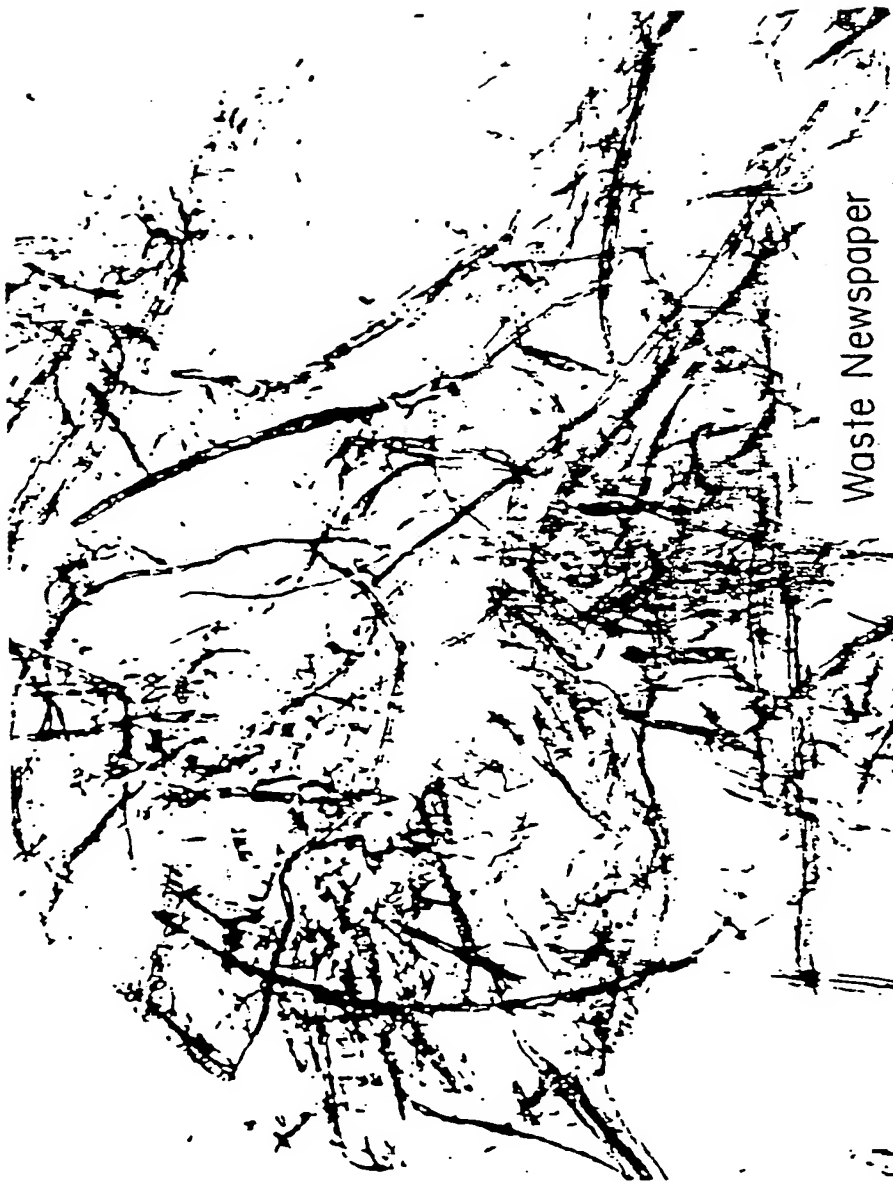


Bamboo

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FIG. 16

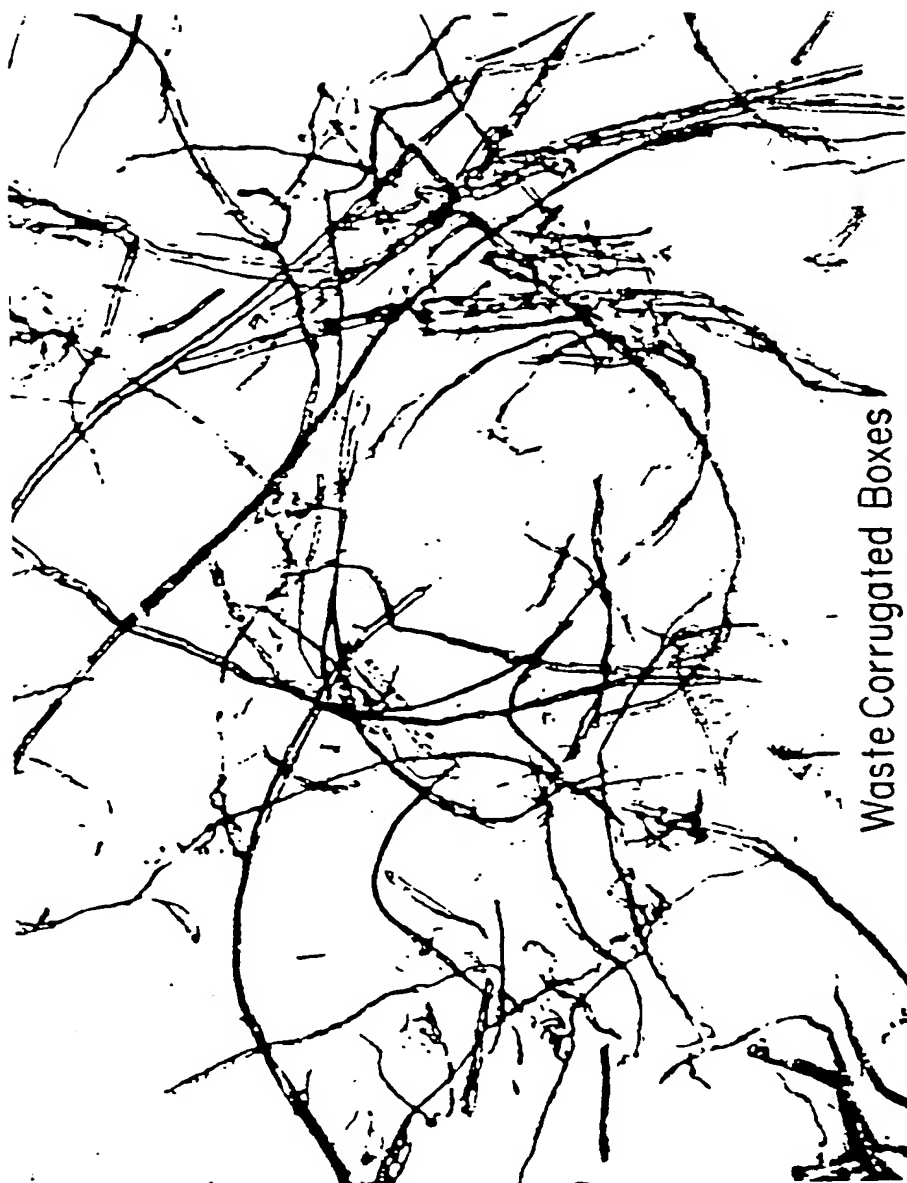


Waste Newspaper

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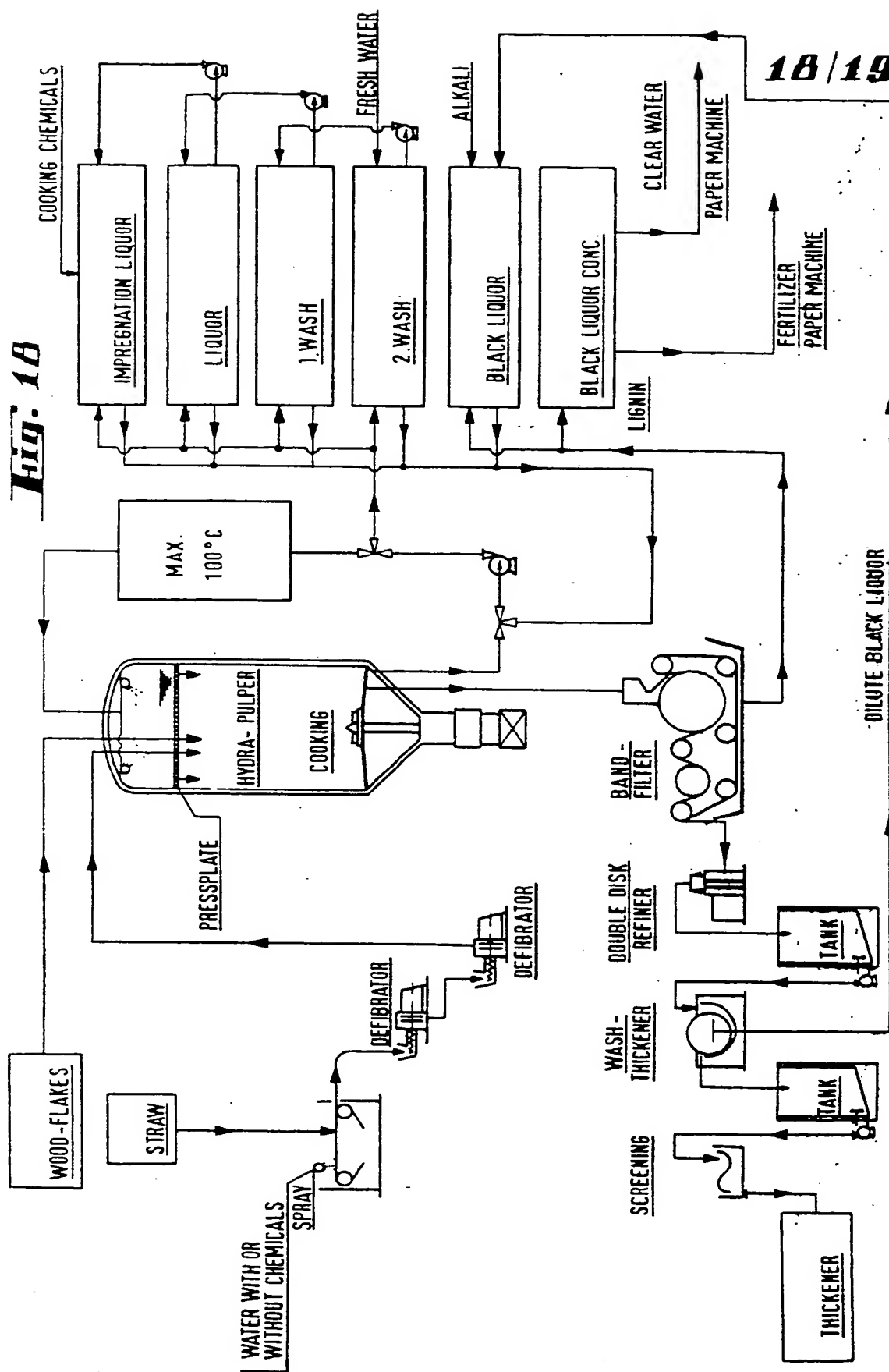


FIG 17



Waste Corrugated Boxes











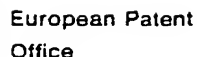
European Patent  
Office

# EUROPEAN SEARCH REPORT

0012775  
Application number

EP 78 10 1794

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, Vol. 39, no.4, October 1968 APPLETON, WISCONSIN (USA) S.A. PUZYREV et al.: "Method of obtaining fibrous materials", page 353, abstract no. 3516 & SU - A - 214 306  * entire abstract *  ---	1,2	D 21 C 3/16 D 21 C 1/00 D 21 H 3/18 A 23 K 1/12 C 05 F 7/02
	FR - A - 2 333 892 (A.G. VAUGUE)  * page 2, line 2 to page 5, line 24 *  ---	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.)
	DE - C - 546 104 (E. SCHMIDT)  * claim 1; page 1, lines 1-48 *  ---	1,2	D 21 B 1/38 D 21 C 1/04 D 21 C 3/16 D 21 C 3/22 D 21 H 3/02 D 21 H 3/18 A 23 K 1/12 C 05 F 7/02
	DE - C - 410 824 (R. WOLFFENSTEIN)  * claim; lines 1-16, 23-28, 42-49 *  ---	1,2	
	DE - C - 307 087 (FELDMÜHLE)  * entire document *  ---	1,3-6	
	FR - A - 1 479 952 (PRINTING PACKAGING & ALLIED TRADES RESEARCH)  * abstract 1,2a,b,d,f,g,h; page 1, right-hand column, lines 5-19; page 2, left-hand column, lines 4-34 *  ---	5,6	CATEGORY OF CITED DOCUMENTS
	US - A - 4 053 645 (J.W. JELKS)  * claims 1-9; drawing; column 2,	1,2,9 ./.	X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			&: member of the same patent family, - corresponding document
Place of search The Hague		Date of completion of the search 25-07-1979	Examiner NESTBY



## EUROPEAN SEARCH REPORT

0012775

Application number

EP 78 10 1794

-2-

EPO Form 1503.2 05.78

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